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The Atmospheric Effects of Stratospheric Aircraft: A Fourth Program Report

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The Atmospheric Effects of Stratospheric Aircraft: A Fourth Program Report

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Chapter 1

Program Summary

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INTRODUCTION

This report marks two important milestones in NASA's recent aviation-related atmospheric research. First, as discussed in later chapters, a new effort has been initiated as an element of the NASA Advanced Subsonic Technology Program to investigate the possible atmospheric impact of subsonic aircraft, particularly the growing commercial fleets. This Subsonic Assessment (SASS) has been combined with the ongoing Atmospheric Effects of Stratospheric Aircraft (AESA) (Stolarski and Wesoky, 1993a) element of NASA's High-Speed Research Program (HSRP) (Williams, 1993) to establish the Atmospheric Effects of Aviation Project (Wesoky *et al.*, 1994). Therefore, future AESA progress reports, which focus on the effects of supersonic or high-speed civil transport (HSCT) aircraft, will be accompanied by similar information on subsonic aviation.

The second important milestone is related directly to AESA. In late 1992, NASA asked the National Research Council (NRC) of the National Academy of Sciences to provide an evaluation of AESA. A panel of ten experts, including four from Europe, received extensive briefings from AESA managers and investigators before an interim assessment report (Albritton *et al.*, 1993) was transmitted to them in June 1993.

This chapter begins with a discussion of the interim assessment and the NRC review. The AESA response to that report (NRC, 1994) is then discussed and related to the 1995 assessment which will end Phase I of the program. Finally, the major uncertainties expected to remain in the post-1995 time frame are discussed and the initiatives for the AESA Phase II program plan are presented.

1993 INTERIM ASSESSMENT FOR AESA PHASE I

The 1993 AESA interim assessment evaluated the potential impact of a fleet of HSCT aircraft on stratospheric ozone. The result depends on size of fleet, Mach number (cruise altitude), and emission index (EI) for NO_x (EI, g of equivalent nitrogen oxides as NO_2 per kg of fuel). Although a realistic jet engine suitable for the proposed fleet of supersonic civil aircraft will not be available until after the turn of the century, laboratory and theoretical studies show great promise for the development of efficient and safe engines with EI as low as 5. For an estimated fleet of 500 Mach 2.4 aircraft flying realistic routes, the calculated effects on the column of ozone is a depletion of less than 1 percent for EI of 5 and as much as 2-3 percent for EI of 15. Table 1 shows the range of predictions included in the interim assessment, along with newer Mach 2.0 results.

Table 1. Assessment Model Predictions

SCENARIOS			ASSESSMENT MODEL						
HSCT FLEET MACH NO.	HSCT EMISSIONS INDEX gm equiv NO_2 /kg fuel	BACKGROUND Cl (ppbv)	COLUMN OZONE CHANGE (%), 40 TO 50 DEG N LATITUDE						
			AER	CAMED	GSFC	LLNL	NCAR	OSLO	
1.6	5	3.7	-0.04	0.69	-0.11	-0.22	-0.01	0.04	
1.6	15	3.7	-0.02	0.48	-0.07	-0.57	-0.60	0.15	
2.0	5	3.7	-0.29			-0.48			
2.0	15	3.7	-0.63			-1.45			
2.4	5	3.7	-0.47	0.38	-0.29	-0.58	-0.26	-0.47	
2.4	15	3.7	-1.20	-0.45	-0.86	-2.10	-1.80	-1.30	
2.4	15	2.0	-2.00	-1.10	-1.30	-2.70	-2.30	-1.90	
2.4	45	3.7	-5.50	-2.80	-4.10	-8.30	-6.90	-3.50	

It was also reported that an increasing body of experimental evidence clearly demonstrates that the lower stratospheric chemistry of NO_x is strongly influenced by heterogeneous reactions occurring on the surfaces of sulfate aerosols. This implies that nitrogen compounds are less active

towards ozone than they would otherwise be, and that ozone loss in the lower stratosphere is dominated by hydrogen and chlorine oxides.

In its recent evaluation report, the NRC (1994) commended AESA for, on the whole, performing good work which has enhanced understanding of atmospheric chemistry, but also recommended that more work will be needed to allow fully informed decisions concerning the environmental compatibility of HSCT aircraft. In response to these recommendations, NASA has augmented the AESA effort as an element of the Phase II HSRP (Williams, 1993; Shaw *et al.*, 1993) that is developing HSCT technology.

In the opinion of the NRC Panel, the three remaining key uncertainties in the AESA studies are: (see page 5, NRC, 1994)

- Dispersion of HSCT emissions in the stratosphere
- Physical and chemical properties of stratospheric aerosols and their precursors
- Possible climate effects of the HSCT fleet

Many AESA program elements were noted to have contributed to a reduction in uncertainties. However, some changes in program structure and emphasis were advised. Among those for which the Panel recommends augmentation of effort are: (see page 6, NRC, 1994)

- Three-dimensional (3-D) (i.e., altitude, latitude, and longitude) chemical assessments, with more attention to incorporating data from satellites
- Parameter space sensitivity studies with two dimensional (2-D) (i.e., altitude and latitude) models
- Examination of HSCT effects on climate, especially those pertaining to water vapor and ozone
- Organic chemistry in the upper troposphere
- Additional independent studies of plume/wake processes

INITIAL RESPONSE OF AESA TO THE NRC EVALUATION

Guidance of the NRC Panel is first being used to focus on activities which can significantly improve the assessment to be provided at the end of AESA Phase I in 1995. In particular, a number of activities have been initiated to address modeling issues brought out in the NRC report. These are being mostly accomplished within the scope of the existing research efforts of current AESA investigators. They include:

- *A step-by-step model intercomparison.* This has been started as a chemistry-only intercomparison with just two of the 2-D models. The intercomparison will then be expanded to include other 2-D models and the trajectory chemistry model used for interpretation of aircraft data. The next step in this comparison will be to define a chemical benchmark using an accurate Gear-type code to integrate the chemical equations at several fixed points with specified inputs. Two detailed radiative models have been intercompared and shown to give virtually identical results (Kawa, personal communication). These will be used as a standard to resolve several outstanding issues in the calculation of photolysis rates in existing 2-D models. 2-D or 3-D chemistry and radiation codes will be tested against these standards.

- *2-D model improvements.* At a recent workshop on heterogeneous chemistry (see Chapter 3), the issues concerning improved parameterizations of particle formation and heterogeneous processes were discussed. An ad-hoc committee of assessment modelers (see Chapter 4) met afterwards to define what improvements should be made and what improvements could be made to 2-D assessment models between now and the 1995 assessment. Because of the differing impacts of NO_x incorporated into a vortex with polar stratospheric clouds (PSCs) and NO_x outside a vortex, it is important to properly represent the conditions under which PSCs form and the exchange of air between the vortex and surrounding region. This means that, at a minimum, a model must account for the fluctuations of temperature around a latitude circle. This will be done by the 1995 assessment. It also means that a credible model should be able to reproduce the observed tracer gradients across the vortex edge and the implied degree of isolation of the vortex region. This can be done with a wave parameterization which has been demonstrated (Garcia *et al.*, 1992) to work in the simplest case of a single wave, but it will be difficult to incorporate a full multiwave parameterization into the assessment models for 1995.
- *2-D sensitivity studies emphasizing exploration of phase space.* Johnston *et al.* (1989) performed a set of sensitivity studies on HSCT perturbations using a one-dimensional model. Tie *et al.* (1994) have recently published a 2-D sensitivity study using gas-phase chemistry. Another recent study (Considine *et al.*, 1994) used a 2-D model incorporating heterogeneous chemistry to calculate the perturbation to ozone caused by NO_x and water from an aircraft fleet which was assumed to deposit all of its effluents at a single altitude and latitude. The model calculated the perturbation for all combinations of 3 different flight altitudes (16, 20, 24 km), 3 flight latitudes (0, 30, 60 degrees N), 3 NO_x emission indices (5, 15, 45 g/kg fuel), 3 chlorine burdens (1, 2, 4 parts per billion by volume), and 3 aerosol surface areas (1, 2, 4 times the estimated background). These calculations showed significant sensitivity to both altitude and latitude of injection, with injections at lower latitudes and higher altitudes giving larger ozone sensitivity. An outstanding issue is whether these gradients in calculated ozone loss are dependent on the known deficiencies in the 2-D model dynamical representation.
- *3-D model calculations.* Thus far, the Phase I AESA program has chosen not to attempt 3-D atmospheric simulations with full chemistry. The strategy has been to do 3-D tracer transport calculations to determine whether any significant corridor effects are expected and to serve as a test of the 2-D parameterizations of stratospheric dynamics (e.g., Douglass *et al.*, 1993). These will be continued with longer time integrations. An important aspect of these studies is to understand the mechanisms responsible for stratosphere-troposphere exchange which determine pollutant lifetimes and the mechanisms for transporting NO_x to higher altitudes where it can more efficiently destroy ozone. The understanding of 3-D effects should benefit greatly from Upper Atmosphere Research Satellite (UARS) data which are now becoming available. These data will be used wherever possible to test and improve models.
- *Effects of sulfur and soot.* It has generally been assumed from approximations that the effects of sulfur and soot in the exhaust of a fleet of HSCTs will not have an important effect on the atmosphere. However, related calculations were not included in the interim assessment where their validity could be carefully scrutinized. The Phase I AESA program will address the issue of calculating the expected effects of sulfur and soot from HSCT exhaust and will document these calculations in the 1995 assessment report, which will include an evaluation of which effects can be safely considered insignificant. The report will also address the issue of whether there are significant studies needed for later assessment reports.

1995 PHASE I ASSESSMENT

The interim assessment (Albritton *et al.*, 1993) has extended the basic findings of earlier international ozone assessments (WMO, 1991) for the effects of stratospheric aircraft. However, many uncertainties still exist, for example, the spreading of the exhaust plume is a complicated and not well understood process. Of particular importance are: the rate of transport of the exhaust downward into the troposphere, and the rate at which exhaust is transported upward to higher altitudes in the stratosphere. The lifetime of exhaust gases is determined primarily by downward transport into the troposphere where soluble forms can be washed out by rainfall. This in turn determines the magnitude to which concentrations of various pollutants will build up. Upward transport to higher altitudes is important because the aerosol concentrations are lower at those altitudes, and ozone is more sensitive to NO_x (i.e., through gas phase chemistry). These uncertainties were highlighted in the interim assessment report, but it is not yet clear how to quantify them.

Input for the interim assessment ended just before the *in situ* atmospheric observations of the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE). The 1995 assessment will incorporate knowledge gained from that aircraft campaign (see Chapter 2) as well as from the later observations of the combined Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) expedition (Stolarski and Wesoky, 1993a). The ER-2 aircraft payload used in these expeditions now contains a measurement of at least one of the radical species in each of the key catalytic cycles responsible for ozone depletion (hydrogen, nitrogen, chlorine, and bromine). The constraints placed on models of stratospheric chemistry by these measurements will be more significant than ever before. In the past, the crucial radicals of hydrogen oxide species (HO_x) had not been simultaneously measured, thus suggesting the possibility that models were seriously in error. The measurement-imposed constraints should allow the estimation of more useful uncertainty ranges than previously possible.

Transport uncertainties remain one of the most difficult aspects of the assessment problem to quantify. Data from SPADE and ASHOE/MAESA will include measurements of carbon dioxide in addition to other tracers such as nitrous oxide, methane, and fluorocarbons. This suite of tracer measurements should place additional constraints on the model dynamics which will reduce the uncertainty range. In addition, tracer measurements from UARS will provide global coverage. During SPADE, measurements were made for the first time of the intensity of the ultraviolet radiation at the aircraft where the radical measurements were being made. These measurements should further constrain the uncertainties in our knowledge of stratospheric photochemistry.

All of these improvements in our knowledge, gained from aircraft field experiments, satellite data, improved and intercompared models, and continued laboratory work, will lead to a significantly improved assessment for 1995. That assessment will be more oriented toward specific problems and uncertainties than the 1993 interim assessment.

It is hoped that the 1995 assessment will be made with sufficient confidence to provide an initial framework for drafting international standards concerning the operation of a fleet of HSCT aircraft. Major gaps in understanding and remaining uncertainties will probably lead to modifications in draft standards before any final international agreement can be reached. The goal for accomplishing a confident atmospheric assessment to support such an agreement has been set for late 1998.

MAJOR UNCERTAINTIES FOR POST-1995

By the time of the 1995 assessment, an understanding of the stratosphere and our ability to model it will have significantly improved. While it is not possible to predict exact uncertainties likely to be remaining at that time, some crucial areas can be identified:

- *Inability to do a fully 3-D assessment.* 2-D models have been the workhorse for the interim assessment and improved versions of these models will still be the primary tool for the 1995 assessment. More emphasis will be given to 3-D simulations in the 1995 assessment, but fully 3-D models with chemistry likely will not be available at that time. Improvements in 2-D models will make them significantly better representations of the atmosphere, but doubts will remain until we are able to make a fully 3-D assessment with models which have been tested extensively against *in situ* and satellite data.
- *No constrained set of radicals for background sulfate aerosol amounts observed.* We are now in the declining phase of the stratospheric aerosol enhancement caused by the eruption of Mt. Pinatubo in June 1991. During SPADE, the aerosol was at a lower altitude than during the Second Airborne Arctic Stratospheric Expedition (AASE-II) (Stolarski and Wesoky, 1993b) and the enhancement was about a factor of 5 above background compared to more than 30 during AASE-II. Further reductions in aerosol amount and peak altitude can be expected for ASHOE/MAESA. By 1997, the aerosol amount should be very near background levels, barring any further major eruptions.
- *No constrained set of radicals for Northern Hemisphere summer.* One of the recommendations of the NRC panel was a Northern Hemisphere summer campaign of atmospheric observations. The summer is when we can expect the greatest buildup of pollutants because of weak stratospheric winds and when the sunlight which drives catalytic destruction mechanisms is also a maximum. In 1997, the aerosol amount should be reduced to near background, making this an ideal time to take the full ER-2 payload into the field in a SPADE-like campaign.
- *Insufficient measurements of radicals and tracers at 20-25 km altitude.* As shown in Figure 1, current predictions indicate that significant ozone depletion resulting from HSCT emissions will occur above the nominal 20 km aircraft cruise altitude. But we are still awaiting our first detailed *in situ* measurements of key radicals and tracers in the region just above flight altitudes for HSCTs (and the sampling altitude of the ER-2 aircraft). These are expected to occur during the initial deployments for the Perseus autonomous aircraft (Russell *et al.*, 1991). It is likely that these measurements will yield surprises and raise new questions. Further flights will be necessary to confirm findings and to understand them well enough that they can be used to reduce uncertainty in predictions of HSCT atmospheric effects.
- *Incomplete set of tracer measurements with which to constrain or reduce transport uncertainties.* In developing a 3-D assessment model, it is a necessity that we have sufficient measurements of key tracers in order to validate the accuracy of the transport in the models. Preliminary investigations using SPADE data indicate the strong potential for the suite of tracer measurements to rigorously test the long-term transport in the models. These measurements need to be extended to other seasons over a wide range of altitudes and latitudes, and covering both phases of the 26-month quasi-biennial oscillation. Combining these measurements with existing radionuclide data should allow a significant reduction in the uncertainty in atmospheric transport.

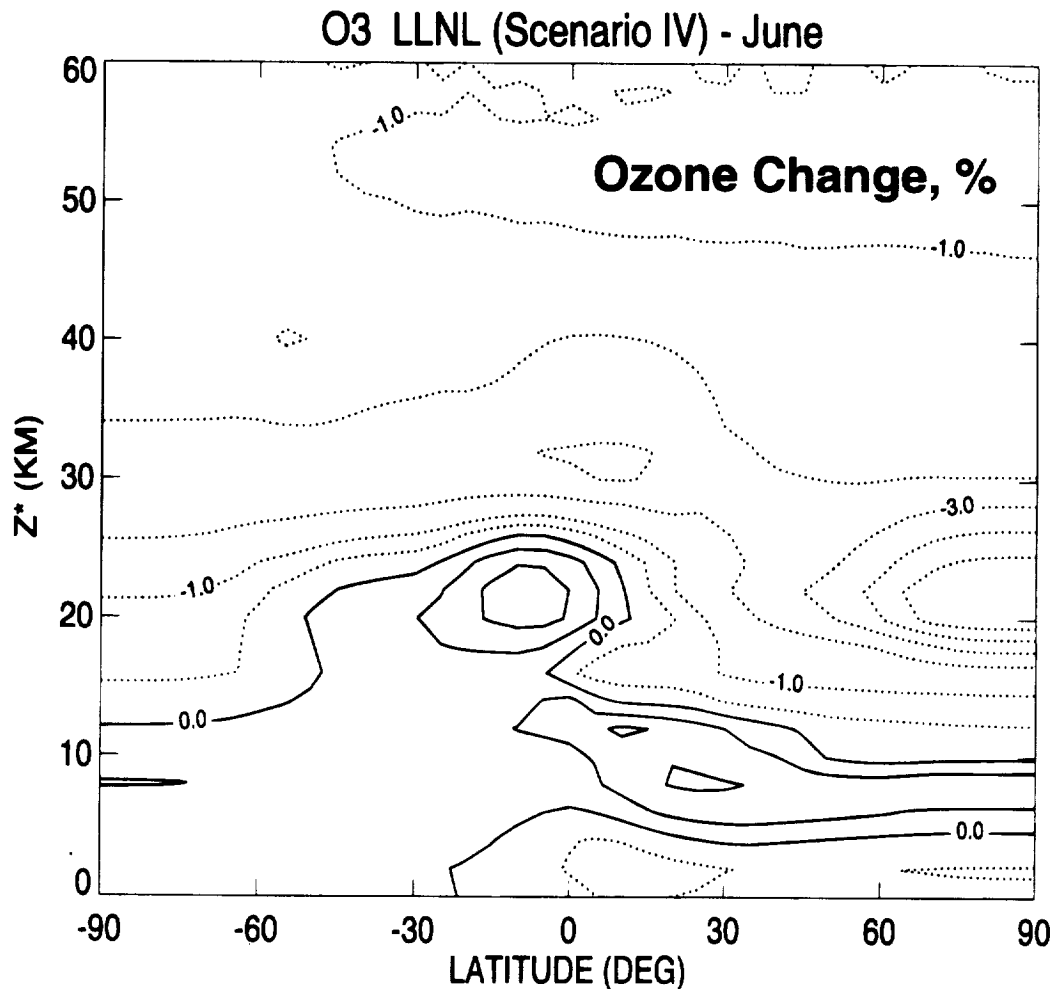


Figure 1. Model-calculated (Stolarski and Wesoky, eds, 1993b) percent change in June 2015 local atmospheric ozone for Mach 2.4, NO_x emissions index of 15. Contour intervals are -4%, -3%, -2%, -1%, -0.5%, 0%, 0.5%, 1%, 2%, 3%, 4%.

- *No measurements of aerosol composition in the stratosphere.* The ultimate test of the application of laboratory work to the understanding of the formation mechanism of stratospheric aerosols is to actually measure their composition *in situ*. During Phase I of AESA, we have supported the development of just such an instrument (Murphy and Thomson, 1994) which can be deployed during Phase II.
- *Inability to fully utilize UARS and Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) measurements to constrain answers above 25 km.* These data sets are now becoming available and will be utilized to the fullest extent possible for the 1995 assessment, but more time and focus will certainly be needed to take full advantage of their content.
- *Insufficient exploration of the possibility of climatic impacts.* By the 1995 assessment, we will have the results from one study (Rind and Lonergan, 1994) which should show the most important potential climatic effects. The Phase II program will need to support a more intensive effort and coordinate closely with SASS.

PHASE II PROGRAM PLAN

As implied above, the NRC report included a number of recommendations which cannot be addressed in the time frame of a 1995 assessment. Further research in the post-1995 time frame (i.e., AESA Phase II) was recommended to increase the level of confidence of any subsequent assessments and to support consideration of HSCT emissions standards. Response to some recommendations generally continues activities begun in AESA Phase I (e.g., 2-D sensitivity studies), while others are being implemented in the newer SASS investigations (e.g., studies of organic chemistry and experimental measurements of interactions between engine exhaust plumes and aircraft vortex wakes). Coordination of AESA with SASS and other programs will be important if a confident assessment is to be attained in a timely manner.

Some special post-1995 activities include:

- *Northern Hemisphere summer mission.* The NRC report recommended a mission in the Northern Hemisphere summer. As shown in Figure 2, previous NASA *in situ* measurement campaigns (i.e., typified here by AASE-II) have emphasized the polar regions in winter, to study the ozone hole phenomena associated with CFCs. The current ASHOE/MAESA campaign, with ER-2 flights over a wide range of latitudes, will add to the latitude database, as did SPADE. But clearly, the recommended measurements in summer at northern latitudes will add significant seasonal and latitude observations to the database. It is planned

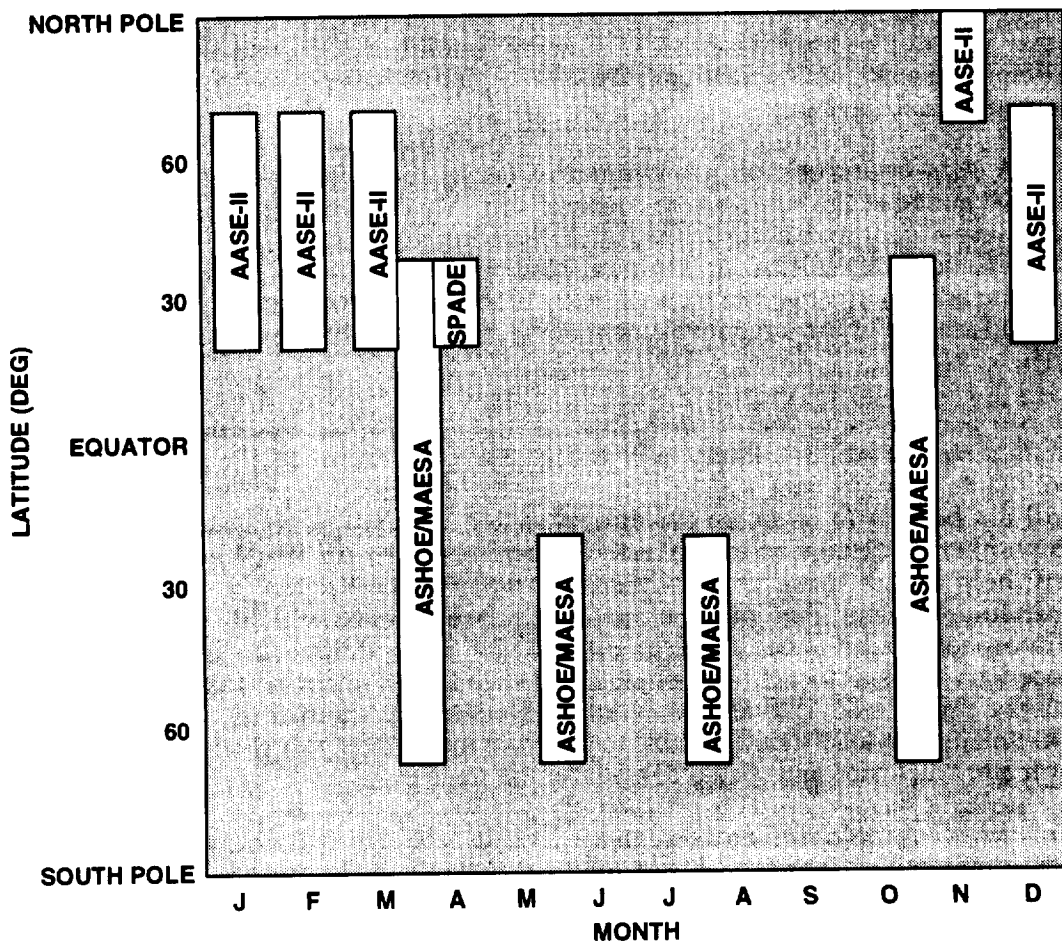


Figure 2. Seasonal and latitudinal extent of recent *in situ* measurement campaigns (excluding test flights).

to conduct such measurements no later than 1997, when we can expect near-normal background levels of sulfate aerosol, making that an ideal time for such a mission. The initial plan is a payload similar to that used in SPADE (see Chapter 2) and ASHOE/MAESA. The mission will be planned in close cooperation with the Upper Atmosphere Research Program. It could be carried out from a combination of sites such as Ames and Fairbanks (i.e., to reach the North pole); or perhaps an east coast site so that the ER-2 could sample the location of the proposed HSCT North Atlantic corridor.

The most important NRC recommendation which could not be addressed in the base program was to reduce the transport uncertainties. To respond to this recommendation, a 3-D modeling initiative and an observation program to obtain the data needed to validate these models have been proposed. Another area of importance which cannot be covered within the base program is the extended measurements of a constraining set of radical species to altitudes above ER-2 level. This will require strong cooperation with and support from the new NASA Environmental Research Aircraft and Sensor Technology (ERAST) program.

Some specific issues to be addressed in AESA Phase II are:

- *3-D modeling initiative.* If we are to have a 3-D assessment by 1998, then a significant investment will have to be made, including enhancement of the infrastructure necessary to support such models. Because of the large amounts of data necessary for testing models and the large amount of results generated by such models, the infrastructure is significantly larger for 3-D models than for 2-D models. This will have to be closely coordinated with other programs (e.g., the Earth Observing Satellite (EOS) and the High-Performance Computing and Communication (HPCC) Program) which are in the process of building up computational capability.
- *UARS data interpretation.* A number of issues raised by current assessments involve understanding of the stratosphere above 25 km. This region is not easily reached for *in situ* sampling except by balloon. It was decided early in the AESA effort that ballooning was an inefficient way to explore this area. Now that UARS data is becoming available, it will provide an important global view of many of the key stratospheric constituents. AESA can take advantage of the large investment being made in the retrieval and interpretation of this data.
- *Tracer measurement survey (including aerosol composition measurements).* The greatest remaining uncertainty likely will be in characterization of the transport of injected pollutants. UARS data will help constrain the dynamical representations in models, but will not be able to focus on the critical region near the tropopause where stratosphere-troposphere exchange occurs. Tracer measurements during SPADE and ASHOE/MAESA will help reduce these uncertainties, but will still be limited in time and space. It is particularly clear that more extensive measurements will be needed in the lower stratosphere, but it is not yet clear exactly what the optimum strategy is for obtaining the necessary measurements. The payload for such flights might be significantly smaller than the one used for SPADE and the Northern Hemisphere summer mission mentioned above. The smaller payload should be able to be flown more frequently to obtain tracer information over a broader time and spatial domain for the same cost.
- *Enhanced high altitude measurements.* Perseus flights will obtain the first ever *in situ* measurements of some species in the tropics between 20 and 25 km. These, and mid-latitude Perseus measurements, are expected to raise a number of important questions. This altitude region is the critical link between UARS measurements and ER-2 measurements. Plans for future deployments in this region are uncertain, awaiting successful Perseus test flights. This is an area where the ERAST program can make a

strong contribution to a successful assessment. However, balloon-based measurements will also be considered as an optional strategy.

- *Synergism with subsonic assessment.* A number of issues have received less attention in this program in order to focus on the primary NO_x/ozone problem. AESA will work closely with SASS so that more emphasis can be given to the climate problem and to tropospheric chemistry. SASS, with some support from AESA Phase II, will put strong emphasis on understanding the issue of contrail formation and possible changes in cirrus clouds. These, along with the climate modeling studies, should provide a clearer perspective on HSCT climate effects relative to subsonic climate effects. The emphasis on tropospheric chemistry in SASS (NO_x budgets, hydrocarbon emissions, etc.) should lead to a significantly better evaluation of tropospheric effects of HSCTs.

SUMMARY

The AESA Phase I program has now been in existence for four years and has produced an interim assessment report. This assessment and the related NRC review have pointed to clear evidence that the ozone chemistry of the lower stratosphere is strongly influenced by heterogeneous reactions on aerosol surfaces. Models incorporating heterogeneous chemistry show significantly reduced sensitivity of ozone to injections of NO_x from a fleet of HSCTs.

The NRC review also emphasized major uncertainties which will remain beyond the 1995 assessment at the end of AESA Phase I. These include potential climate effects, transport rates for injected pollutants, inaccuracies inherent in the approximations of 2-D assessment models, and the absence of extensive northern mid-latitude constituent measurements during summer.

To respond to these and other questions, an augmented AESA program plan has been developed for Phase II of HSRP. This program is to run from 1995 through 1998, with the goal of providing the scientific basis for regulating the operations of any potential HSCT fleet. Primary new initiatives in the program are: a series of tracer transport mini-missions, a 3-D modeling initiative, and a northern hemisphere summer mission.

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Chapter 2

Stratospheric Photochemistry, Aerosols and Dynamics Expedition

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This chapter has been prepared on behalf of investigators of the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE), which was based at the NASA Ames Research Center, Moffett Field, California, in late-1992 and early-1993. An ER-2 aircraft was used as the instrument platform, primarily for stratospheric observations (see enclosed configuration drawing). SPADE was the first expedition dedicated specifically to the objectives of the High Speed Research Program (HSRP); in particular, for obtaining data to help assess the potential impact of future fleets of high speed civil transport (HSCT) aircraft on the atmosphere. The mission played an important role in the continuing development of the ER-2 instrument suite for stratospheric observations; hitherto, principally sponsored by NASA's Upper Atmosphere Research Program (UARP).

OBJECTIVES

1. To study chemical processes potentially affecting ozone, at altitudes most strongly influenced by stratospheric aviation, by making comprehensive measurements of radicals and reservoir species, including HO_x radicals (OH and HO_2) and NO_2 , for the first time from the ER-2, along with NO, NO_y , ClO, O_3 , HCl, sulfate aerosols, and UV and visible irradiances. The mission included night, sunrise, day, and sunset (i.e., diurnal) observations over California and northern and southern survey flights to provide a rigorous diagnosis of factors regulating concentrations of radicals.
2. To examine distributions of tracers whose concentrations in the lower stratosphere vary on time scales, ranging from months to years. These studies provide essential data for analyzing dispersal and eventual removal of aircraft exhaust emitted into the lower stratosphere.
3. To determine the effects of heterogeneous chemistry on concentrations of radicals and reservoir species, by obtaining data for various stages of decay of the Mt. Pinatubo aerosol, and by examining morning-evening differences.
4. To lay the groundwork for 1994 HSRP and UARP field missions.

SCIENCE TEAM

Instruments:

P. Wennberg/ J. Anderson	Harvard University	High Altitude OH Experiment (HO_x)
D. Fahey	NOAA/Aeronomy Lab	Reactive Nitrogen (NO/NO_y)
J. Elkins/ D. Fahey	NOAA/Climate Monitoring and Diagnostics Laboratory	Fast Response CFC-11 and CFC-113 Airborne Chromatograph for Atmospheric Trace Species (ACATS)
K. Kelly	NOAA/Aeronomy Lab	Lyman-Alpha Hygrometer (H_2O)
M. Loewenstein/ J. Podolske	NASA/Ames	Airborne Tunable Laser Absorption Spectrometer (ATLAS)
M. Proffitt	NOAA/Aeronomy Lab	UV-Absorption Ozone Photometer (O_3)
C. Webster	NASA/JPL	Aircraft Laser Infrared Absorption Spectrometer (ALIAS)

J. Wilson	University of Denver	Focused Passive Cavity Aerosol Spectrometer (FPCAS) and Condensation Nucleus Counter (CNC)
K. Boering/ S. Wofsy	Harvard University	High-Sensitivity, Fast-Response CO ₂ Analyzer
J. Dye/ D. Baumgardner	National Center for Atmospheric Research	Forward Scattering Spectrometer Probe (FSSP)-300 Aerosol Spectrometer
R. Stimpfle/ J. Anderson	Harvard University	Multiple Axis Resonance Fluorescence Chemical Conversion Detector for ClO and BrO
R. Chan	NASA/Ames	Meteorological Measurement System (MMS)
C. McElroy	Atmospheric Environment Service/ Canada	Composition and Photodissociative Flux Measurement (CPFM)

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OPERATIONAL HISTORY

The SPADE instrument payload was among the heaviest and most complex flown by NASA's ER-2. Owing to the difficulty of integrating this payload, the mission was divided into two phases: an extended test phase in October and November 1992, and a brief test phase followed by operational flights in April and May 1993. Analysis of the results indicated that important information on stratospheric transport rates could be provided by observations of seasonal variations of CO₂ in relation to other long-lived tracers (principally N₂O). Consequently, a brief follow-up mission, with the payload consisting of tracer instruments only (N₂O [ATLAS], O₃ [NOAA], H₂O [NOAA], ALIAS, and CO₂ [Harvard]), was flown in October 1993, to capture the seasonal variations and provide a context for Airborne Southern Hemisphere Ozone Experiment observations.

In the fall of 1992, test flights showed that the payload exceeded ER-2 constraints on both total fuselage weight and center of gravity, requiring significant weight reductions by fuselage instruments prior to operational missions in the spring. Tests of concepts for diurnal flights demonstrated the need for simplified flight plans. Valuable data sets were collected for comparison with previous and subsequent observations.

By the time of the spring mission, weight reductions made to O₃, MMS, H₂O, and HO_x instruments, with considerable effort by the instrument teams, brought the payload below the total fuselage weight constraint. Although the center of gravity met design limits, aircraft performance was unacceptable in turbulent conditions, forcing deletion of the Microwave Temperature Profiler (a piggyback investigation) and the telemetry package from the payload.

The spring operational phase achieved all mission objectives. In addition, on several occasions, the ER-2 observed the composition of polar air at the end stage of winter chemistry and its own wake (allowing measurement of the NO_x emission index for the ER-2 engine at cruise conditions).

The SPADE mission tested a number of concepts that underlie the stratospheric models used for assessing HSCT effects on the stratosphere. In some cases these concepts appear to be sound, some appear doubtful (i.e., further analysis required to determine the significance of observed discrepancies), and some clearly need to be revised.

PRELIMINARY RESULTS

1. The new HO_x instrument performed reliably with excellent signal-to-noise ratio, apparently free of artifacts. The measurements showed that reactions of HO_x represent

the dominant pathway for catalytic recombination of O_3 at ~ 20 km, with the reaction $HO_2 + O_3 \rightarrow OH + 2O_2$ accounting for more than half of ozone removal. These results require a re-ordering of previously accepted ideas for the relative importance of HO_x , ClO_x , and NO_x catalytic cycles for ozone loss in the lower stratosphere. The data imply a greater role than expected for enhanced O_3 loss associated with volcanic aerosols, and may help explain the long-term reductions observed for mid-latitude O_3 . An abrupt increase in HO_x radicals was observed at visible sunrise, coincident with appearance of NO from photolysis of NO_2 (Figure 1a). This phenomenon appears to reflect photolysis of 20-30 ppt of HONO (Wennberg *et al.*, 1994; Cohen *et al.*, 1994); however, significant production of this highly-reactive species is not predicted from known photochemical reactions. Analysis using a data-assimilation model showed that the observations were consistent with production of HONO from heterogeneous decomposition of HNO_4 on aerosol particles ($HNO_4 \rightarrow HONO + O_2$) (Figures 1b, 1c, [Salawitch *et al.*, 1994; Michelson *et al.*, 1994]).

Significance for HSRP: The first systematic observations of stratospheric HO_x radicals (OH and HO_2) achieved a capability for atmospheric chemistry vigorously sought for more than 20 years. The results confirm some general features of the models used to predict effects of HSCTs on the atmosphere, but significant discrepancies emerged, elucidated by careful analysis of the comprehensive suite of measurements made in SPADE. In particular, currently accepted chemistry predicted higher sensitivity of O_3 loss rates to NO_x additions than observed. This result would tend to reduce the computed impact of HSCT operations at 18-20 km in the volcanically-perturbed atmosphere of 1993. The remarkable capability of the SPADE payload to define key catalytic cycles demonstrates that such observations could help address, to first-order, major questions attaching to impacts of HSCTs on the atmosphere. Clearly, measurements should be repeated when the concentration of volcanic aerosols is closer to "background." To date, we don't have any observations in the principal source regions for global ozone (i.e. in the tropics at altitudes between 22 and 28 km, and in regions of possible large-scale removal, e.g., polar regions in summer [National Academy Report]). The SPADE results indicate that observations in these regions could provide essential underpinning for assessments of potential HSCT effects.

2. In spring, and in each fall campaign, data for CO_2 exhibited very low scatter when plotted against data for other long-lived tracers, such as N_2O . Relationships were uniform throughout the hemisphere in each season, but changed markedly between each set of seasonal observations. Atmospheric motions smoothed out latitudinal variations, in less than three months, and the stratosphere responded as single entity to changing concentrations of CO_2 in the troposphere below. The data characterize propagation through the stratosphere of the signal representing seasonal changes and long-term trends in tropospheric CO_2 . The observations allow us to diagnose rates for vertical transport of stratospheric trace gases. Near the tropopause, at subtropical latitudes, the signature of recent input of CO_2 and H_2O from the troposphere into the stratosphere was clearly observed (Figure 2, Boering *et al.*, 1994). Transport of the CO_2 signal into the middle stratosphere occurred during winter only. Most importantly, the lifetime inferred for gases emitted into the stratosphere (e.g., by HSCTs) was longer than represented in current models, due to a bottleneck near the tropopause, but exchange from lower altitudes/middle latitudes with high altitudes/tropics was faster than in two-dimensional models (Figure 3, [Boering *et al.*, 1994; Wofsy *et al.*, 1994]).

Significance for HSRP: One of the most difficult aspects of assessing aircraft perturbations is to determine the validity of the transport properties of the models (National Academy Report). The addition of the CO_2 instrument to the ER-2 payload provides a unique tracer for transport, covering time scales from a season to more than

five years. The impacts of HSCTs on O₃ may be larger than indicated in present models if, as inferred from the CO₂/N₂O relationships, the residence time for exhaust of HSCTs is longer and more exhaust is transported to higher altitudes (Figure 3, Wofsy *et al.*, 1994). Examination of model runs (HSRP annual report, 1992) shows that computed perturbations to O₃ are inversely related to the computed lifetime for the exhaust. The observations apply only to 1993, coincident with the largest perturbation ever observed to hemispheric O₃. The mean age of air in the middle stratosphere, as determined from the CO₂ concentration, was about five years, and observations over that time frame, with seasonal resolution, are evidently required to define the lifetime and distribution for HSCT exhaust. The eventual effects of HSCTs on stratospheric O₃ depend critically on the quantity of NO_x transported to high altitudes, especially in the tropics, where most global ozone is generated. The SPADE data provide tantalizing indirect indications of transport rates to this region. Definitive information requires direct measurements of CO₂-tracer relationships in the principal ozone-forming region (tropics, 20-28 km), strengthened by data from the summer pole and other potential source regions. The potential for obtaining definitive results on transport rates from tracer measurements complements the applications of radical measurements to the ozone question, in that the atmospheric regions and time scales that should be examined are similar and, at this writing, not accessible.

3. Diurnal variations of NO, NO₂, HO_x, and ClO were observed in experiments that successfully followed radical concentrations through sunrise and sunset in air parcels with equivalent tracer concentrations. Measurements (including NO₂, for the first time, by the ER-2 (Jaegle *et al.*, 1994) and solar irradiance [McElroy, 1994]) provide a nearly-complete set of chemical data to critically assess current understanding of gas-phase and heterogeneous reaction rates in the stratosphere. The results demonstrate the importance of reflection of sunlight from clouds in regulating radical concentrations, and they suggest that improvements are needed in model treatments of solar ultraviolet irradiance for low sun angles (i.e., solar zenith angles of more than 85 degrees).

Significance for the HSRP: One of the best tests of present understanding of the chemistry of ozone-destroying radicals in the stratosphere is to observe concentration changes when the sun rises or sets. The SPADE measurements provided the most complete radical measurement set to date. Because of the completeness of this set of measurements, along with observations of associated ultraviolet light, aerosols, and tracers, the possible explanations for deviations from model predictions are severely constrained. When analysis is complete, the data should increase confidence (i.e., decrease uncertainty) in predicted ozone perturbations resulting from aircraft emissions.

4. The anomaly in measured HCl concentrations first observed during the earlier Airborne Arctic Stratospheric Expedition II (AASE-II) (i.e., low values of HCl relative to expectations from photochemical models) was confirmed. The cause remains obscure, with possibilities including incorrect specification of total inorganic chlorine (Cl_y), missing or incorrect chemistry, or unknown instrument artifacts.

Significance for HSRP: Several suggestions have been put forward to explain the HCl results. These include a possible pressure dependence in the chlorine partitioning which manifests itself as a dependence on altitude. Recent laboratory results suggesting such a dependence in the photolysis rate of chlorine nitrate (ClONO₂) leads to changes in the partitioning in the correct direction when included in models, but cause other problems of understanding. One model calculation indicated that a worst-case impact may be that the HSCT perturbation could be similar to low atmospheric chlorine scenarios (i.e., an approximate doubling of ozone depletion predictions). Until the cause of this anomaly is understood, it is difficult to make any more definitive statements concerning its impact.

5. The volcanic aerosol from Mt. Pinatubo was observed to have aged and settled over the winter season, providing new information needed to understand the evolution of stratospheric aerosols after a major eruption. Measurements of NO, ClO, O₃, NO₂, NO_y, and aerosol surface area confirm the influence of heterogeneous hydrolysis of N₂O₅ on sulfate aerosols in the subtropics. Concentrations of ClO, and the ClO/HCl ratio, declined as the aerosol surface area declined, while NO_x, and the NO_x/NO_y ratio, increased.

Significance for HSRP: Heterogeneous reactions on sulfate aerosols are the key to present model calculations which predict relatively modest impacts of HSCTs on stratospheric ozone at low altitudes. The aerosols from Mt. Pinatubo provided a large enhancement in the surface area available for reaction. SPADE measurements were made when the Mt. Pinatubo aerosol surface area had decreased significantly from its maximum of 30 times background during AASE-II. The surface area during SPADE was still approximately five times background. These data will help us to map out the dependence of radical concentrations and ozone chemistry on the aerosol surface area.

6. Dynamical and chemical signatures of the ER-2 wake were observed several times during SPADE. The payload provided both CO₂ and H₂O, as combustion indices, and the partitioning of NO_y into NO and NO₂ in the plume was determined, allowing remarkably complete characterization of aircraft exhaust products approximately ten minutes after emission. The emission index (EI) at cruise was 3-5 g NO₂/kg fuel, consistent with Pratt & Whitney's estimates for the J75 engine for cruise conditions (Figure 4 and Table 1, Fahey *et al.*, 1994). Coincidentally, this is the range currently being sought for advanced engines intended to power future HSCTs.

Significance for HSRP: A potential uncertainty in the evaluation of HSCT effects is whether the emission indices measured in ground tests are those which will actually occur at cruise in the stratosphere. During SPADE, several observations were made of the ER-2's wake. The measured EI for NO_x appears to confirm that data from ground tests can be directly utilized in modeling calculations (see Fahey *et al.*, 1994). Flight measurements of the ER-2 exhaust, also indicate the possibility of such observations contributing to the understanding of near-field interaction (i.e., between the aircraft wake and exhaust) effects on global chemistry, by demonstrating successful strategies for measuring wake chemistry of operational aircraft.

REPORTING

A workshop was conducted in September 1993 to discuss the results from SPADE and AASE-II and to form teams for preparing scientific publications. As a result, a set of linked publications is being developed to interpret and communicate results in a coherent and concise manner.

Major topics to be addressed include:

- Chemical cycles in the lower stratosphere
 - Radical families and ozone recombination rates
 - Diurnal studies and reservoir species
- Aerosols in the lower stratosphere
- Photochemistry in the lower stratosphere

- Chlorine chemical cycles and budget
- Polar air chemistry
- Stratospheric transport and tracer fields
- Aircraft exhaust
 - Locating at cruise altitude
 - Measurement of plume structures and emission indices

The scientific publications will be part of a special issue of *Geophysical Research Letters*, and some will appear also in *Science* and *Journal of Geophysical Research*.

Table 1. Observations during plume encounters*

Encounter Date		1 May 3, 1993	2 May 7, 1993	3 May 18, 1993
GMT	(s)	71715	103520	62690
Lat.	(deg)	15	37	46
Long.	(deg)	-118	-125	-116
Duration	(s)	9	10	5
Age	(s)	630	470	600
P	(mbar)	65	48	62
T	(K)	197	213	214
O ₃ ^a	(ppmv)	0.52	2.44	1.68
ClO ^b	(ppbv)	0.009	0.005	0.025
J _{NO2} ^b	(s ⁻¹)	0.016	0	0.014
ΔNO	(ppbv s)	2.60	----- ^c	1.74
ΔNO ₂	(ppbv s)	-----	4.47	-----
ΔNO _y	(ppbv s)	3.50	5.55	3.36
ΔCO ₂	(ppmv s)	3.12	4.19	2.55
ΔH ₂ O	(ppmv s)	4.34	5.00	2.94
ΔH ₂ O/ΔCO ₂	(mole/mole)	1.4	1.2	1.2
ΔNO _y /ΔCO ₂	(10 ⁻³ mole/mole)	1.12	1.33	1.32
EI NO _x ^d	(g (kg fuel) ⁻¹)	3.6	4.3	4.3
Pratt & Whitney estimate	(g (kg fuel) ⁻¹)	3.7 (± 1.4)	3.7 (± 1.4)	3.7 (± 1.4)
NO ₂ /NO ^e		0.20	----- ^c	0.83
ΔNO _x /ΔNO _y		0.89	0.80	0.95
ΔCN	(# (mg air) ⁻¹ s) ^f	1930	210	270
ΔCN/ΔCO ₂	(# (mg air) ⁻¹ /ppmv) ^f	619	50	106

* ppmv = parts per million by volume, ppbv = parts per billion by volume, Δ = the integrated abundance within the plume encounter. Integrations are done with a rectangular method. The H₂O peak is extrapolated to fit the CO₂ peak before integration.

^a Value of O₃ observed in the plume. The lifetime of NO in reaction with ambient O₃ in the plume events is 490, 90, and 100 s, respectively.

^b Used in photochemical steady-state expression for NO₂/NO ratio

^c Measurement in local darkness when NO is zero due to lack of photolysis of NO₂

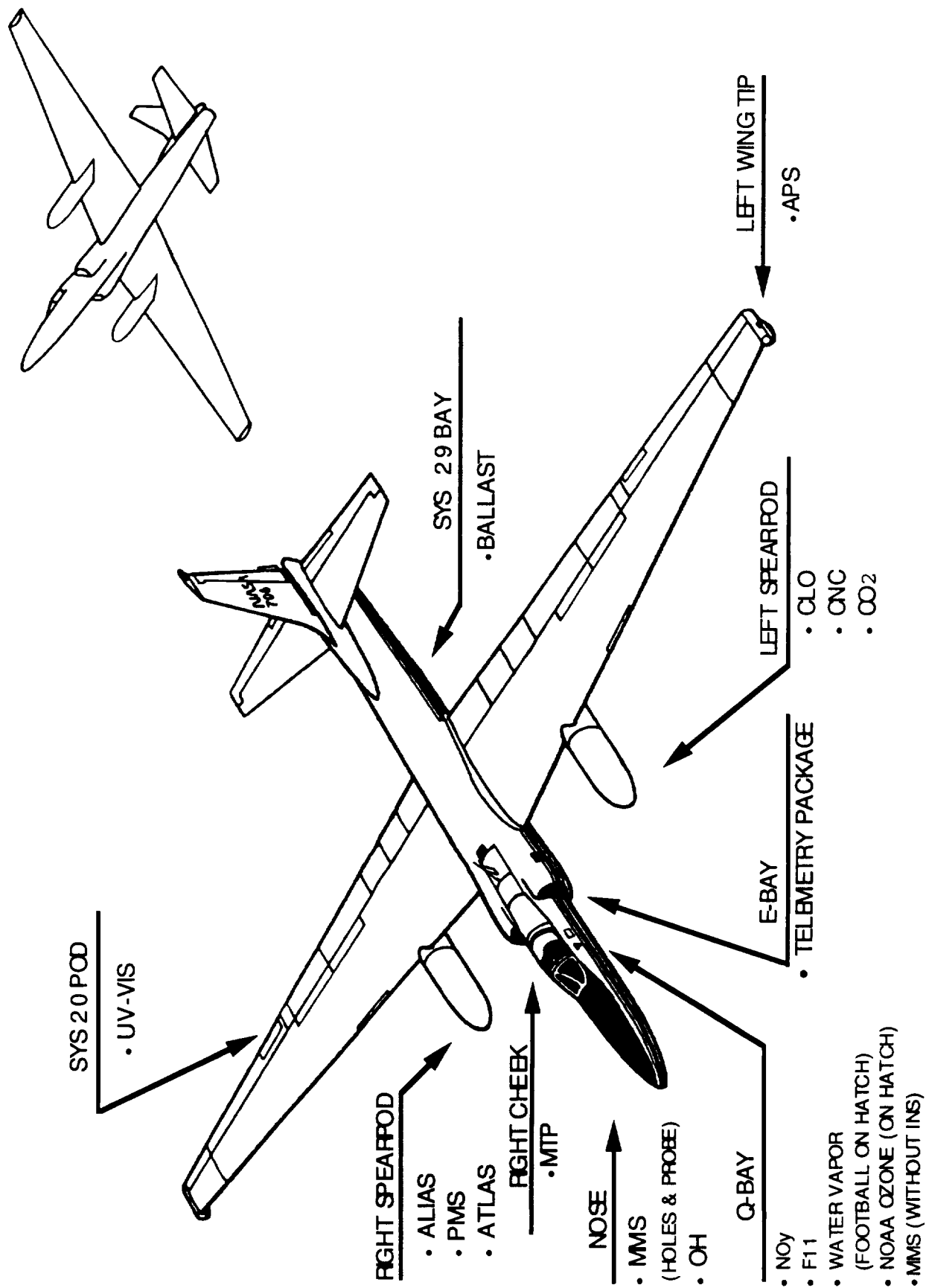
^d $EI_{NO_x} = (46/44) EI_{CO_2} (\Delta NO_y / \Delta CO_2) 10^{-3} \text{ (g (kg fuel)}^{-1})$
 $EI_{CO_2} = 3092 \text{ g (kg fuel)}^{-1}$ for ER-2 cruise conditions (Pratt & Whitney estimate)
 $= 3142 \text{ g (kg fuel)}^{-1}$ for complete combustion

NO_x is expressed as the equivalent mass of NO₂ (46)

^e Photochemical steady-state calculation for plume conditions [Kawa *et al.*, 1992]

^f Unheated inlet line

SPADE CONFIGURATION



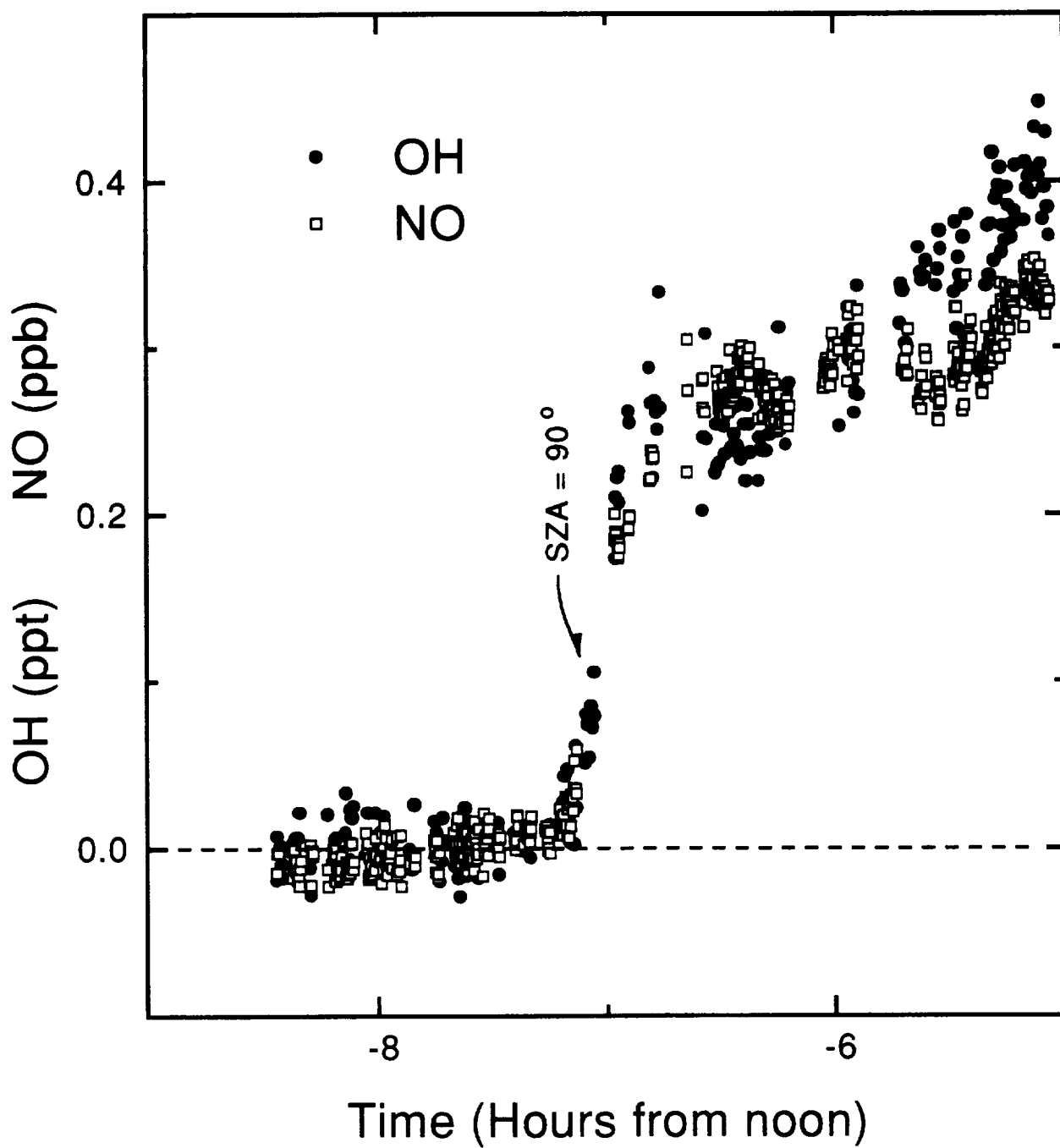


Figure 1a. Rise of OH and NO at sunrise over California, May 1993 (Wennberg *et al.*, 1994).

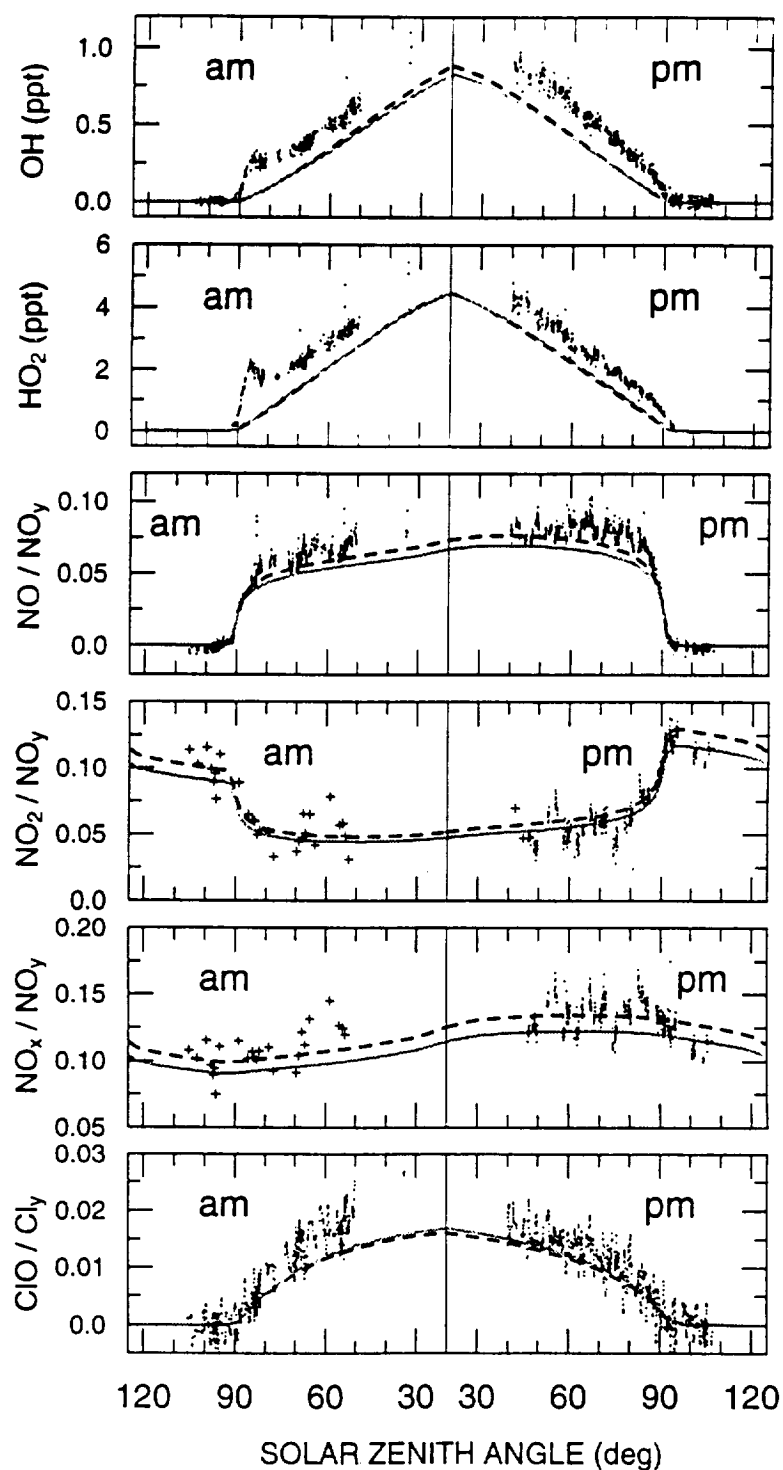


Figure 1b. Radical concentrations computed for a diurnal cycle at 18 km over California in May 1993, compared to observations using the rates constants recommended by DeMore *et al.*, (1992). The model assimilates observed total column ozone and local concentrations of NO_y, O₃, and other long-lived species and it computes radical concentrations (Salawitch *et al.*, 1994). The flights maintained nearly constant concentrations of long-lived tracers by selecting flight trajectories using the Goddard meteorological assimilation model (Seabloom *et al.*, 1994).

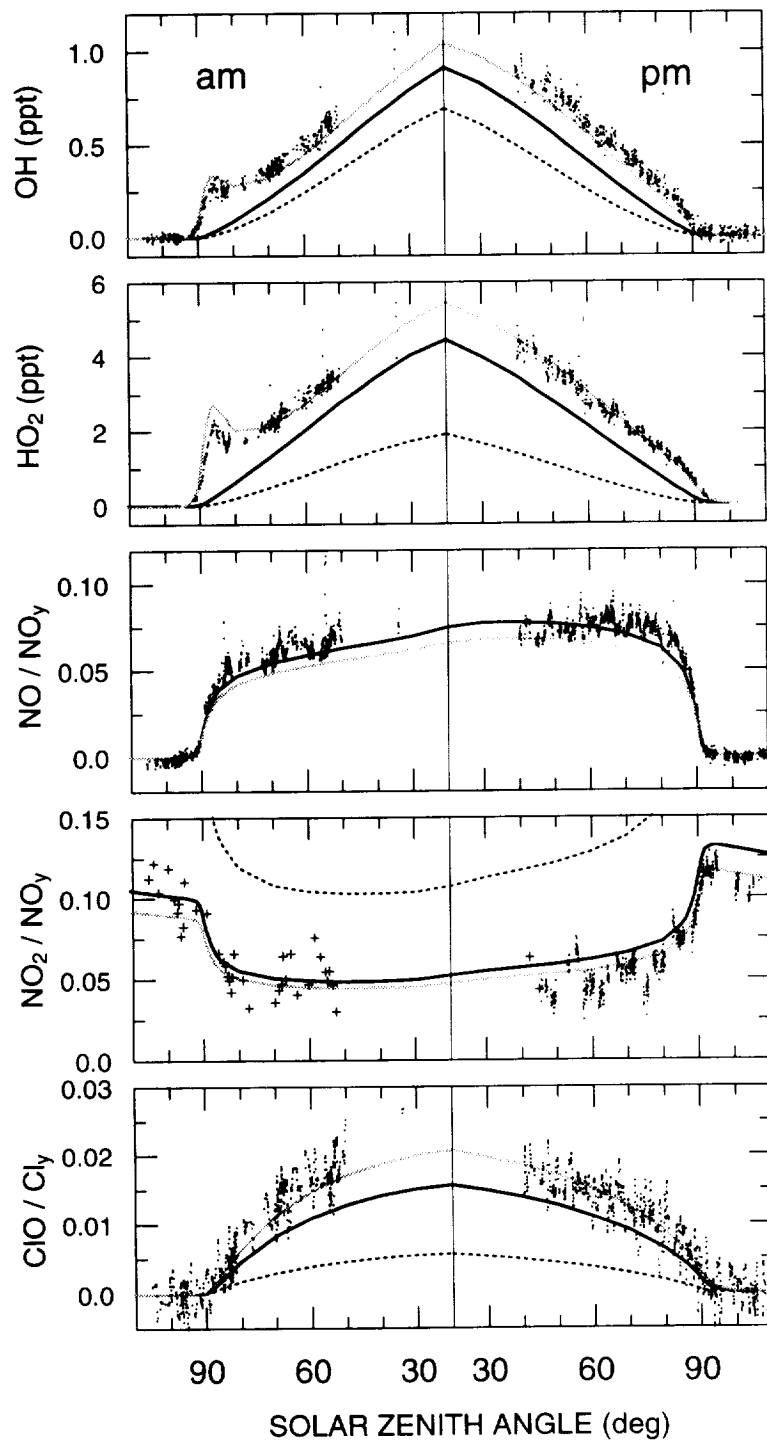


Figure 1c. Radical concentrations computed for a diurnal cycle at 18 km over California in May 1993, compared to observations using the rate constants modified, as described, in the text. Note the simulation of the sunrise burst of HO_x (Salawitch *et al.*, 1994).

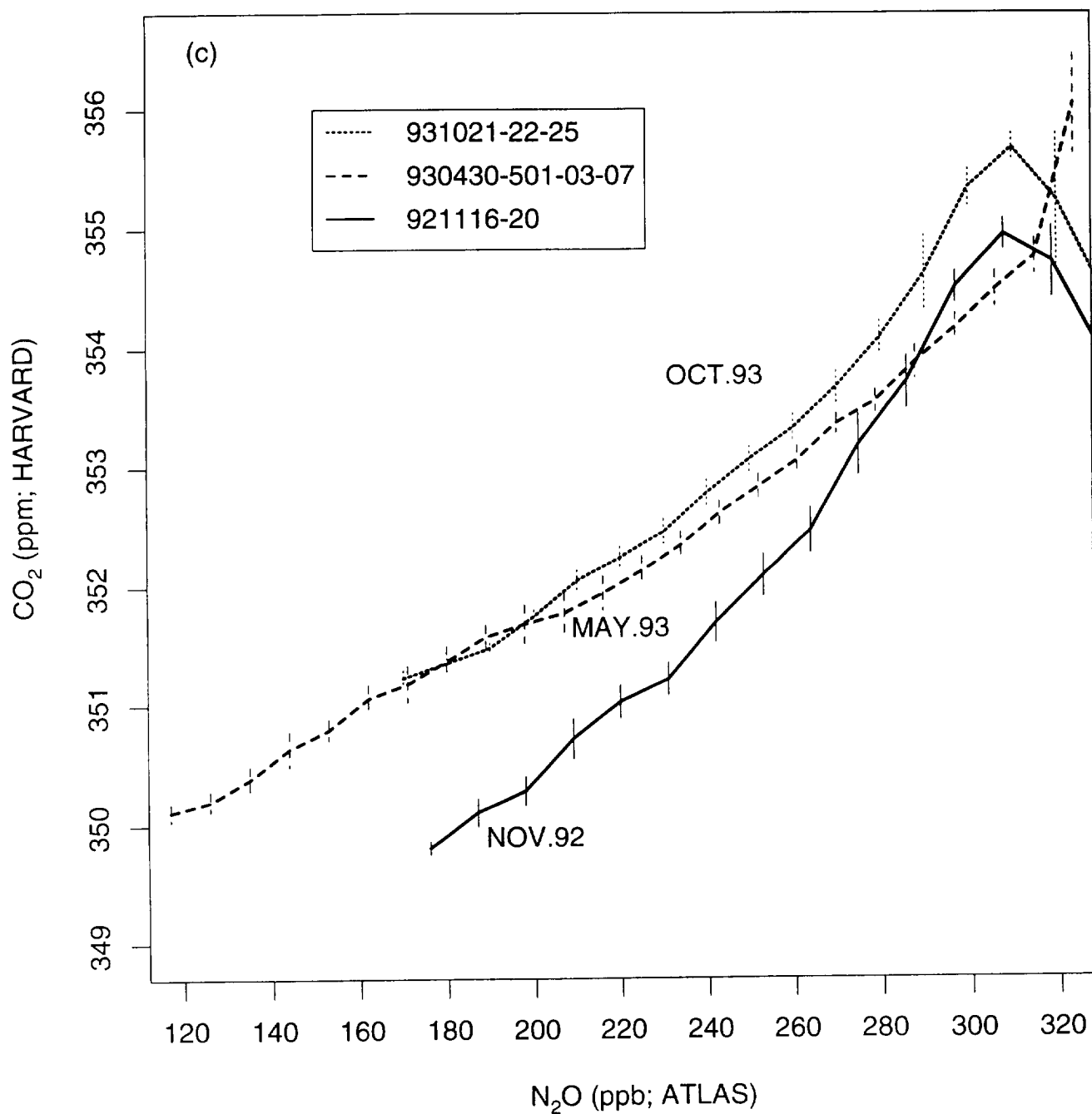


Figure 2. Observed relationships between CO₂ and N₂O in three missions, approximately six months apart, binned and averaged according to the concentration of N₂O (Boering *et al.*, 1994; error bars denote 1 σ).

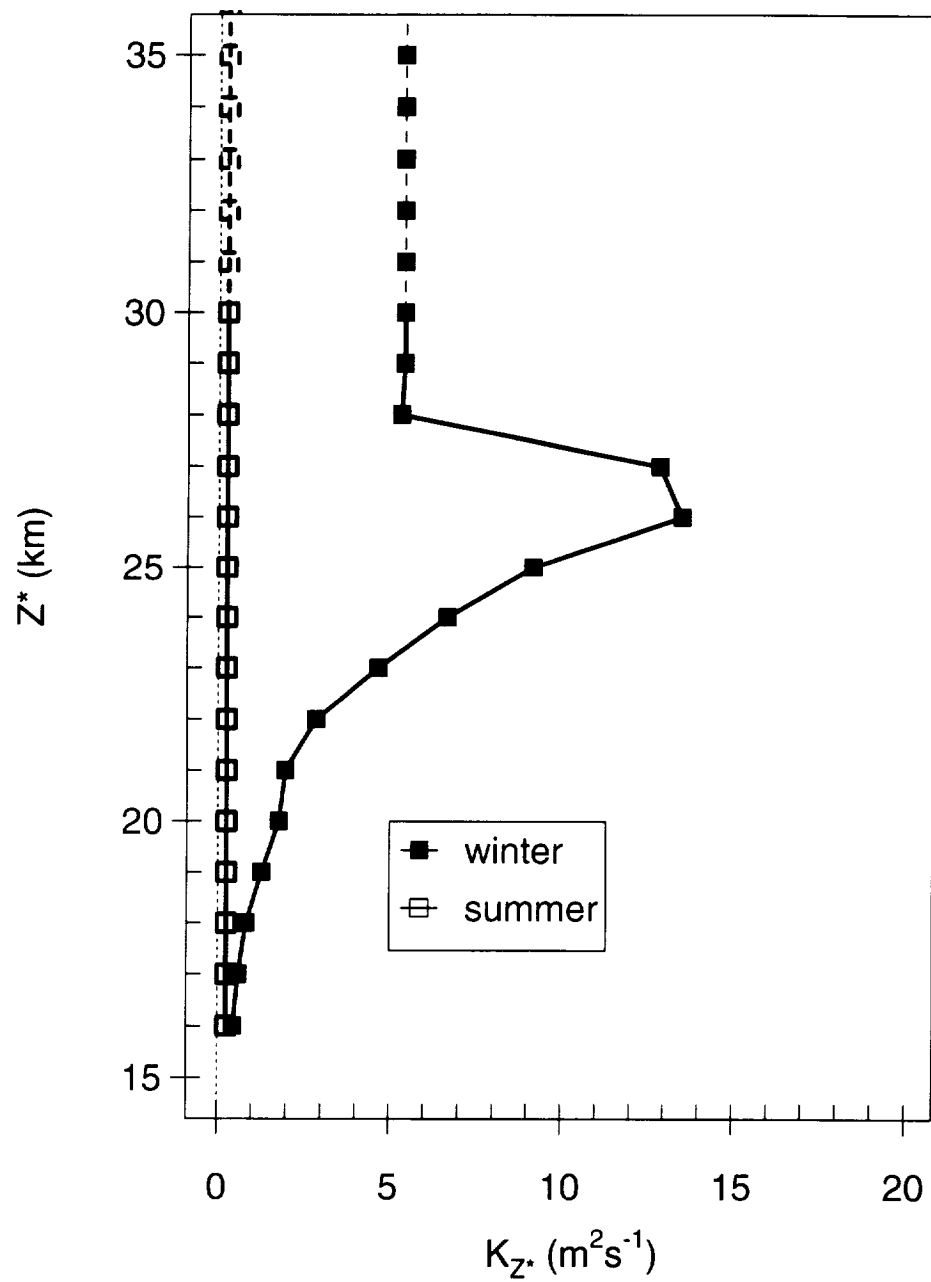


Figure 3a. Inferred mean vertical transport coefficient, from the data in Figure 2 (Wofsy *et al.*, 1994).

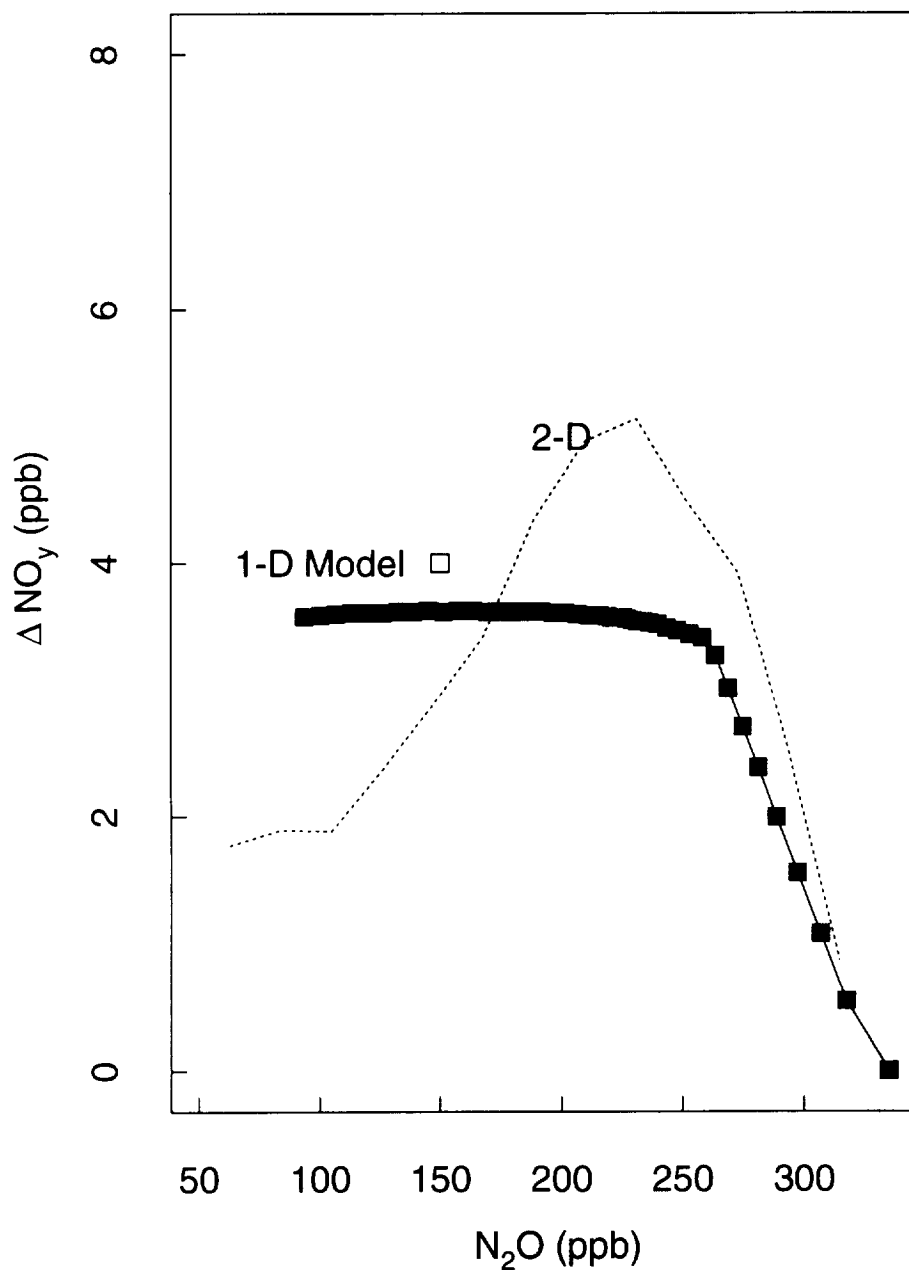


Figure 3b. Calculated distribution for HSCT exhaust, as a perturbation on background levels (scenario EI=15, Mach 2.0), computed with the mean vertical transport coefficient in Figure 2 and with a two-dimensional model that agrees well with observed N₂O-CO₂ relationships. The peak concentration and high-altitude concentrations are notably higher than for current two-dimensional assessment models (see NASA Reference Publication 1313).

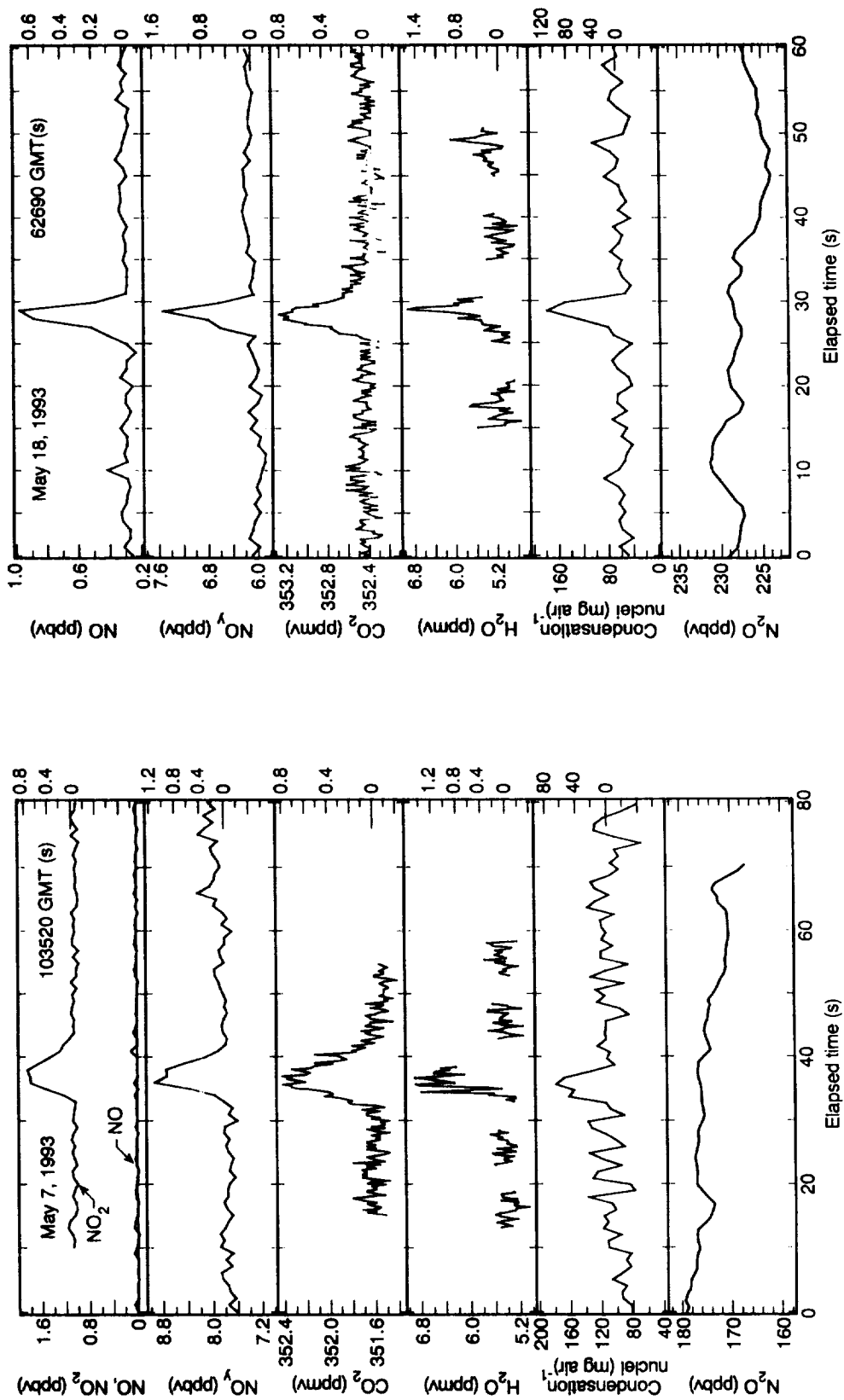


Figure 4a, b. Perturbations to trace gas concentrations observed during the ER-2 crossing of its own wake (Fahey *et al.*, 1994).

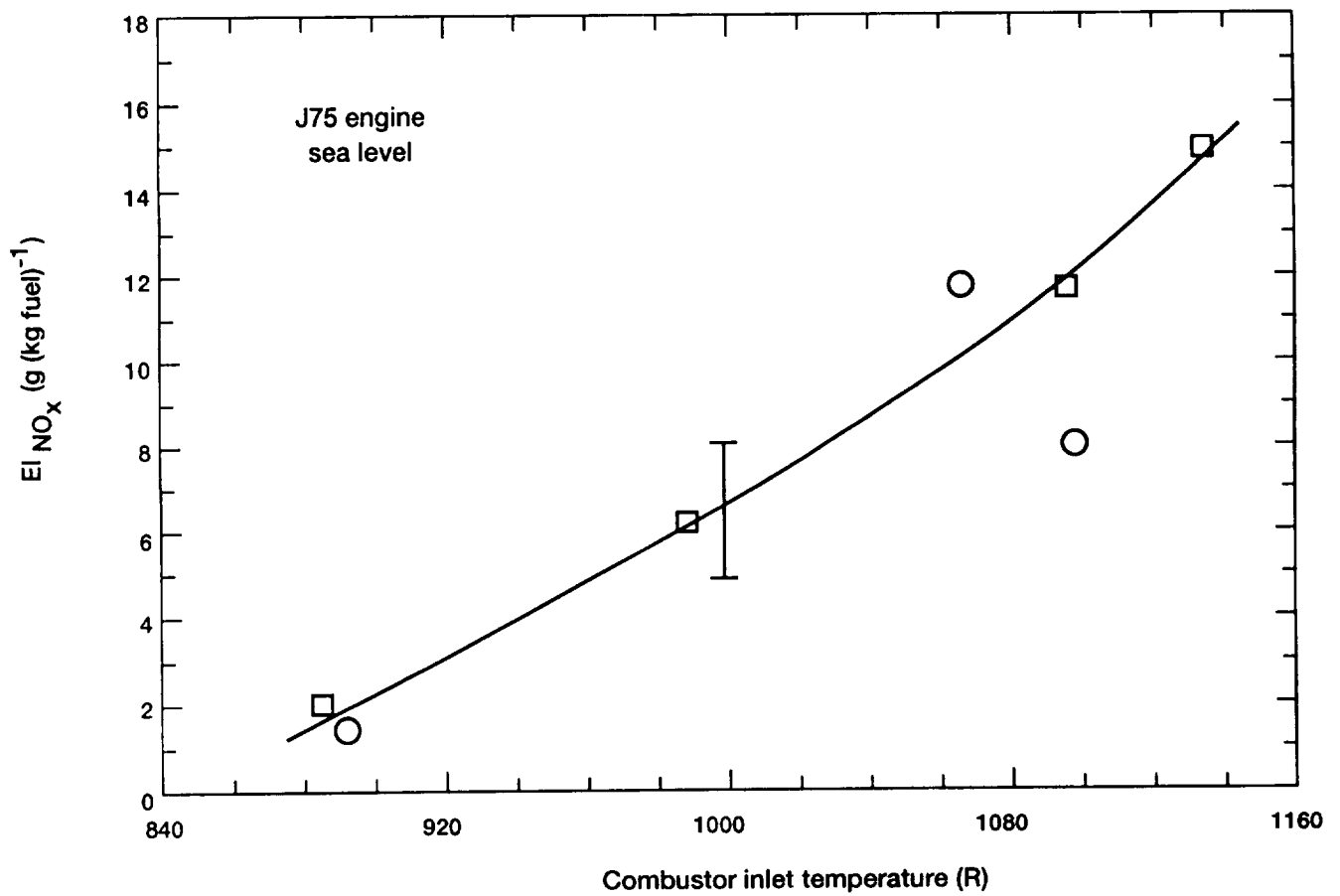


Figure 4c. Prediction of ER-2 emission index based on scaling of ground tests on the JT75 engine (Fahey *et al.*, 1994).

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Chapter 3

Heterogeneous Chemistry in the Atmosphere: An Assessment of Current Status

Report from the Workshop Held in Boulder, Colorado
November 8-10, 1993

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EXECUTIVE SUMMARY

The abundance of stratospheric sulfur is mostly controlled by unpredictable volcanic activity. Even though it will not be possible to predict the exact level of sulfur at a given time in the future, the range of values that are most likely to be present can be ascertained from measurements in the past.

Although it is not currently possible to accurately predict the level of aerosols for a given injection of sulfur compounds into the stratosphere, improvements in our understanding of the microphysics should enable prediction upon further research.

The level of sulfate aerosols in the "clean" stratosphere (i.e., absence of volcanic injections for a long period) and its secular trend, if any, are unclear. However, tropospheric emissions of sulfur compounds are expected to maintain a significant "background" level to facilitate heterogeneous chemistry, even in the prolonged absence of volcanic eruptions.

In the absence of our ability to predict stratospheric sulfate loading, satellite and other observations have to be used. Assessment calculations will have to be carried out under various scenarios such as volcanic, background, etc.

The composition of supercooled liquid sulfuric acid droplets, which make up the particulate, in most of the stratosphere, most of the time, follows thermodynamic predictions if the temperature is above ~ 215 K. Hence, the composition of stratospheric sulfate aerosols can be predicted if T and H₂O vapor (and other vapor) pressures are known.

The temperature and other conditions (e.g., dissolution of gases) required to freeze the sulfate aerosols and to melt the frozen droplets are unclear. Reactivity of frozen sulfate is different from that of the supercooled liquid, and its formation may be a prerequisite for solid polar stratospheric cloud (PSC) formation. Hence, these conditions have to be better quantified.

What we consider Type I PSCs are, at least in some cases, ternary liquid solutions; this possibility has to be assessed. Currently, however, it is impossible to predict when, where, and to what extent PSCs are formed.

- Nucleation of Type I PSCs may occur well below the thermodynamic threshold (i.e., requires supersaturation in HNO₃). Supersaturation appears to be close to 1 in the Antarctic, while it can be 10 in the Arctic. More observations are needed to characterize and find out the reasons for these differences.
- Nucleation appears to depend on the temperature history of the sulfate aerosols upon which PSCs are formed.

Formation of Type II PSCs appears to be critical for denitrification of the stratosphere. The exact conditions that lead to this process are unclear.

In the absence of our ability to accurately predict PSC formation, the use of observations to obtain a present-day climatology for modeling calculations appears to be a reasonable approach. To make this approach robust, more observations, especially at the edges of the vortices, are needed. Further laboratory, field, and modeling studies are needed to develop the capability to better predict PSC formations.

Because the rate of chemical reactions on PSCs are sufficiently fast, and the reactive uptake coefficients for the reactions of HCl with ClONO₂ and HOCl do not depend on the composition of PSCs, chlorine activation rates may be calculated reasonably well inside the vortices.

of PSCs, chlorine activation rates may be calculated reasonably well inside the vortices. However, calculation of activation rates at the edges and outside the vortices, requires better definition of the number and composition of PSCs and the reactive uptake coefficients on them.

The major reactions in supercooled sulfuric acid aerosols can be treated in models using parameterizations. Further laboratory studies are required to better quantify the physical and chemical quantities that go into the parameterizations.

Current stratospheric models use very simplified parameterizations of heterogeneous reactions. Such parameterizations mask microphysical and chemical details. Such details may be essential in the future assessments.

Current models use zonally-symmetric temperatures and species concentrations. They do not include any "special" coupling of the polar vortices to the mid-latitudes and they ignore PSC processes. These assumptions and omissions can lead to significant errors in calculated rates of various processes. The effect of this on assessing effects of aircraft emission should be examined.

Process modeling, which addresses the above omissions and quantifies their contributions, is needed before the next assessment to at least qualitatively judge the consequences of the assumptions and omissions.

There is no systematically collected data on the number, composition, phase, and size distribution of upper-tropospheric aerosols. Such information is crucial to the chemistry of this region.

Because of their expected ubiquity and the complexity of chemical species in the troposphere, heterogeneous reactions are likely to play critical roles in the chemistry of this region. Attempts to model this role have shown heterogeneous chemistry to be extremely important.

The role of aerosols and cloud droplets in oxidant formation and removal is likely to be very important. The role of transition metals in this area is also poorly defined, though it is suspected to be important. The upper-tropospheric ozone levels are likely to be greatly influenced by heterogeneous chemistry.

OBJECTIVES AND LOGISTICS OF THE HETEROGENEOUS CHEMISTRY WORKSHOP

Heterogeneous chemistry is now known to play a very important role in transforming chemical species in the atmosphere. The discovery of the Antarctic ozone hole and the recognition of the role played by reactions on polar stratospheric cloud (PSC) particles have made this field a critical area of intense research. Recent work has shown that heterogeneous processes on sulfate aerosols, which makes up the majority of stratospheric condensed matter in the sub-polar regions, are important.

How does heterogeneous chemistry affect the assessment of the effects of aircraft emissions? This question was the reason for the workshop. The workshop focused on those elements of heterogeneous chemistry that pertain to the effects of aircraft, both supersonic aircraft flying in the stratosphere and subsonic aircraft flying in the lower stratosphere/upper troposphere (LS/UT).

The majority of the workshop dealt with supersonic aircraft related issues (i.e., pertaining to the stratosphere). This is because there has been a tremendous amount of effort expended by the community in past few years towards understanding this issue and we have to take stock of the situation to carry out, in the next few years, a credible and valid assessment of the effects of supersonic aircraft. The issue of the influence of subsonic aircraft on the planet's atmosphere is rather new. In addition, unlike the supersonic transport (SST) aircraft, one needs to be concerned much more about the impact of subsonic aircraft on the troposphere. The research programs that are being tailored to address subsonic aircraft issues are just taking shape. Therefore, the key scientific and policy questions, related to the subsonic program, need to be defined. For this reason, discussion on subsonics centered around currently perceived needs.

It is clear that we could not look at aircraft-related issues without understanding the chemistry in the "background" atmosphere. Hence, a balance was struck in emphasizing both the understanding of stratospheric ozone loss and assessing the possible impact of aircraft on this changing "background."

Clearly, atmospheric chemistry is a multi-disciplinary research area. Yet, there are some distinctions that can be made to facilitate focusing on specific problems and attacking certain key issues that are of paramount importance to the aircraft issue. A simplified chart of this concept is given in Figure 1. There are key questions that can be associated with specific sub-disciplines. It is clear that the surface area, volume, number, location, and composition of atmospheric particles (PSCs, sulfate aerosols, and other particles) are needed to predict the effects of aircraft. In addition, once this information is available, we need the rates of relevant chemical processes on, or in, these different types of particles. Assimilation of these two pieces of information can be used interactively between laboratory studies, field measurements, and modeling calculations to forge out a realistic, tested model of heterogeneous chemistry. Once such a model is available, it can be used as a part of larger assessment models.

In this workshop, three of the four "circles" in Figure 1 were addressed. They fall into three broad categories:

1. What is the climatology of the particles in the atmosphere? What is the composition of the particles? To a first approximation, this boils down to knowing the surface area per unit volume of air and then categorizing the particles into ice, sulfate, or other types.
2. How are the particles formed and removed from the atmosphere? The major uncertainties in this area are those relating to the microphysics of particle formation, coagulation, and removal. The uncertainties in transport also contribute.
3. What are the rates of chemical processes on different substrate? The sub-questions for this area are:
 - Are laboratory studies carried out on the right substrates, at the right concentrations, in the absence of making measurements in the atmosphere on particles present there? If not, how can laboratory studies be made applicable?
 - How can these laboratory-measured rates be reduced to forms that can be used in models?

The fourth area, which is a critical part of any atmospheric chemistry program, is the field observations aimed at understanding processes. Field observations form a reality check of our understanding of reactions that occur in the stratosphere. The chemical processes, directly or indirectly, alter the composition of the atmosphere and the changes are detectable. Atmospheric observations of these changes are extremely important aspects of atmospheric chemistry and are

also a key factor in enhancing and understanding the chemistry itself. This topic, though central to the issues of the workshop, was not directly addressed, because it is a vast area of research and the recent findings have been well documented in a series of papers (e.g., Airborne Antarctic Ozone Experiment [AAOE], *J. Geophys. Res.*, 94, #D9 and D14, 1989; Airborne Arctic Stratospheric Expedition [AASE], *Geophys. Res. Lett.*, 17, #4, 1990; Airborne Arctic Expedition II [AASE II], *Science*, 261, August 27, 1993). However, it was assumed that the participants and the readers are aware of the progress in this area. Whenever necessary, reference is made to these field observations.

Even though the aircraft issues are, for the most part, not centered around the unusual chemistry in the polar vortices, it is imperative to study and understand PSCs. This is because we do not clearly understand the reasons for the observed decadal high- and mid-latitude ozone losses and the contribution to these losses by polar processing. The polar regions may directly export ozone-poor air into high latitudes or export highly-activated air masses, which can destroy ozone at high- and mid-latitudes. Further, changes in the high-latitude chemical composition, at least in areas flown by aircraft, can lead to the formation of PSC-like particles with the consequent denoxification and chlorine activation. Therefore, in this workshop, PSCs were treated on an equal footing with sulfate aerosols.

Currently, it is believed that the role of stratospheric particles in directly changing the radiation balance is not very large when the particle loading has not been enhanced by volcanic eruptions. The primary effect of stratospheric particles is believed to be due to changes in the composition of the gas-phase species via their reaction and/or removal from the gas phase. On the other hand, the particles in the troposphere are believed to change the radiation budget. Thus, the presence of particles in the atmosphere can profoundly affect climate via direct intervention in the radiation balance and/or via changes in the concentrations of greenhouse gases in the atmosphere. Even though this issue is likely to be of paramount importance in the future, the radiative forcing by atmospheric particles were not addressed here. This workshop focused solely on the chemical changes.

The workshop centered around summary talks given by experts, followed by short presentations on specific topics. Both types of presentations were followed by a great deal of discussion. Our understanding of various issues are fragmented and are viewed as being uncertain to different extents. Yet, to be pragmatic, attempts were made to categorize our current knowledge into what is known, what is suspected, and what is unknown. Attempts were made to air controversies and differences in a scientific form. At the end of the workshop, attempts were made to list what is needed, both in the short and long term.

The next section includes the summaries of each individual session, as compiled by the experts (rapporteurs) and as edited by the organizers. The appendices include a list of acronyms, the meeting agenda and a list of attendees, and summaries of the individual talks.

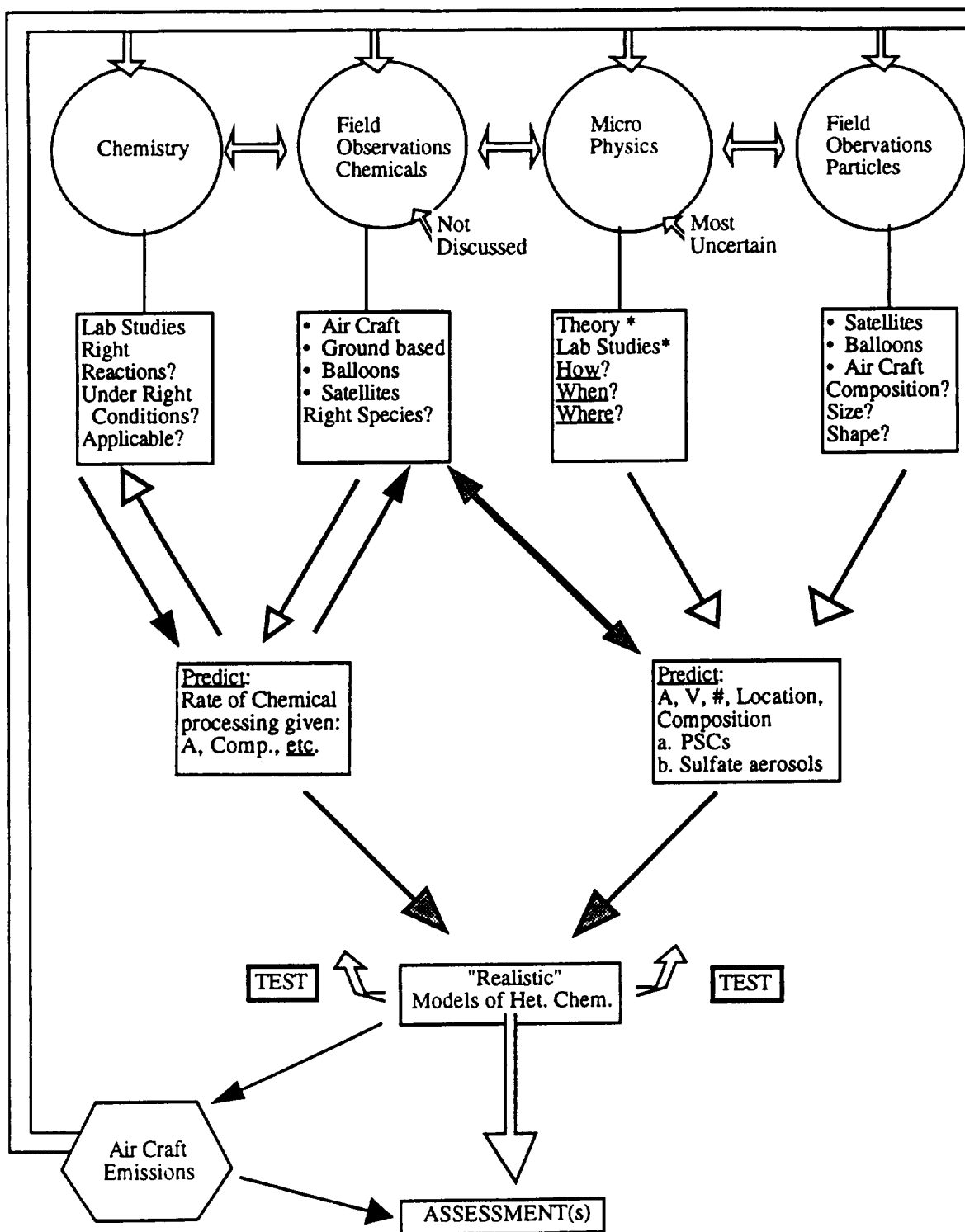


Figure 1. A flow chart for the development of a realistic and reliable model for assessing the impact of aircraft on atmospheric ozone levels.

SUMMARIES OF INDIVIDUAL SESSIONS

CLIMATOLOGY OF STRATOSPHERIC PARTICLES: SIZE, NUMBER, VOLUME, AND AREA

Session Chair: David Fahey
Rapporteur: Chuck Brock
Principal Speakers: Lamont Poole and Terry Deshler
Other Contributors: Matt Hitchman, Chuck Wilson, Jim Dye, and Thomas Peter

It appears that we cannot currently predict the surface area, volume, and numbers of particles in the stratosphere from "first principles," even if the levels of SO₂ are known. This is because particle formation rates are highly non-linear processes and the microphysics of how particles are formed is not known accurately enough for atmospheric purposes. Also, we cannot accurately predict the rates of particle removal from the atmosphere because of our deficiency in understanding atmospheric transport. However, we do know the rates of particle formation in the stratosphere following volcanic eruptions. This knowledge comes from observation and can place reasonable bounds on the rate of particle formation processes. The majority of stratospheric particles are derived from sulfur. It appears that they are either sulfuric acid droplets or formed with a core of sulfuric acid. Therefore, the source of stratospheric sulfur is a crucial factor. The major source of sulfur in the stratosphere appears to be volcanic activity, which cannot be predicted. Therefore, we can not predict the exact level of sulfur in the stratosphere and cannot calculate the aerosol density, surface area, etc. Yet, by using "history" (i.e., observations), we can place limits on the sulfate loading and the available surface area in the stratosphere. Thus, climatology of stratospheric particles has become an important and necessary piece of needed information. Of course, this information is also needed to explain past changes and test modeling of the present atmosphere. Lastly, it is clear that at no time will the stratosphere be devoid of sulfate aerosols and, hence, heterogeneous reactions will always be important. This is because there is always a constant and small, but atmospherically significant, flux of sulfate precursors to the stratosphere from the troposphere. This sulfur flux is consistent with the levels of sulfate observed in the prolonged absence of significant volcanic activity, such as in the 1960's.

During this session, our current observational understandings of the number, surface area, distribution, and composition of the stratospheric aerosols were discussed. Specifically, the observables that we need to know for assessment activities were stressed. They are:

- Number, surface area, and volume density
- Particle size distribution
- Particle shape
- Composition, including major components and trace impurities, density, physical phase (i.e., solid, liquid, etc.), and optical absorbance (refractive index)
- Formation regions (and processes), vapor pressures, nucleation and growth rates
- Sedimentation rates
- Geographic distribution and variability; climatology

Broadly speaking, there are two types of observations that provide information about the surface area of particles in the stratosphere. They are remote sensing, ground- and satellite-based

measurements, and *in situ* observations from balloon or aircraft. In addition to surface area, information on the physical state (i.e., solid vs. liquid) and the nature (i.e., PSCs vs. sulfate aerosols) of the particles and relative humidity are needed to calculate the rates of heterogeneous reaction in the stratosphere. Remote sensing is, for the most part, from satellite and lidar observations. (On occasion aircraft based remote observations have also been carried out [Kinne *et al.*, 1989]). *In situ* observations are from balloon and aircraft data. The observations and interpretation of these data were the major focus of this session.

Remote Sensing

Satellite Observations of Aerosol Extinction: Satellites have provided records of aerosol extinction. These include Stratospheric Aerosol Measurement (SAM) II, from 1978 to 1994, with only sporadic observations after 1990; Stratospheric Aerosol and Gas Experiment (SAGE) I, from 1979 to 1981; and SAGE II, from 1984 to present, which has four aerosol channels.

Each satellite instrument included an extinction measurement at a wavelength near $1\ \mu\text{m}$, so the record at this wavelength is fairly continuous, even though the platforms have changed (except for a gap in data outside the polar regions from 1981-1984). The $1\ \mu\text{m}$ extinction correlates well with aerosol surface area density, but saturates at a value near $40\ \mu\text{m}^2\ \text{cm}^{-3}$. Figure 2 shows the variation of extinction of $1\ \mu\text{m}$ radiation versus the estimated surface area of the particles. Since extinction varies linearly with surface area, the climatology of the surface area for the past decade can be deduced from the extinction data set. However, because of the limited coverage by satellites in the polar regions (due to the orbits and availability of sunlight), information about polar particles is limited, especially during certain times of the year. The derived surface areas have been "validated" by comparisons with balloon-borne particle counters, lidars, and ER-2-based instruments. Therefore, satellite extinction can be used as a surrogate of aerosol surface area to give spatial and temporal variations. The relationship between extinction and surface area is believed to be robust to approximately 20 percent over a variety of size distributions.

Satellite observations have led to the information given below:

1. Satellite measurements of extinction, as a function of temperature, are consistent with the expected swelling of liquid H_2SO_4 , as the temperature decreases, due to the uptake of water (See Laboratory Studies of Heterogeneous Processes). The data look similar for a variety of times, in both tropic and polar regions.
2. Satellite data provide some evidence for an annual cycle of advection of material from the polar vortex, before the vortex breaks down, at a potential temperature $\bar{\theta}$ of 400 K (Thomason and Poole, 1993). At $\bar{\theta} = 500\ \text{K}$, the influence of the Ruiz, Kelut, St. Helens, and El Chichon volcanoes is visible in the satellite record. The vortex areas appear to be cleansed, in terms of extinction, at the end of the winter. It is not known what fraction of "cleansing" in the vortices is due to subsidence and what fraction is due to sedimentation. It is also not known why the cycle in extinction, evident in the vortices, is less regular in the Arctic than in the Antarctic. The variance about the zonal mean in the extinction measurements shows the input of the volcanic eruptions that have occurred in the tropics. The effects of volcanoes on variance about zonal mean damps out within approximately six months. The variance about the zonal mean, in extinction in the polar regions, is high near the vortices and is partially due to the orbit of the satellite and scarcity of data. At $\bar{\theta} = 650\ \text{K}$, a tropical reservoir is apparent in the extinction data, and the effects of the quasi-biennial oscillation (QBO) can be seen. There is a signature of material transport that is in phase with planetary wave activity in the mid- and polar latitudes (Trepte *et al.*, 1993).

3. Satellite extinction measurements in the polar regions have been used in evaluating PSC formation (Poole and Pitts, 1994). From satellite data, an envelope of extinction, as a function of temperature, has been developed for sulfuric acid aerosols. At $T < 200$ K, points inside of this envelope are identified as PSCs. With such distinctions, SAM II data in the Antarctic show the following:
 - June: maximum PSC frequency of occurrence is 0.25, near 22 km and between -45 to 0 degrees longitude. This closely corresponds with minimum temperatures, interpolated from gridded hemispheric data sets.
 - July: maximum frequency reaches ~0.7 at the same location.
 - August: maximum frequency reaches ~0.8 at the same longitude, but is at a slightly lower altitude.
 - September: maximum frequency is at lower altitudes (~15 km), but the stratosphere is warming from above and the frequencies have decreased at these altitudes. There is less zonal variability in the frequency of PSC formation.
 - October: maximum frequency is only ~0.3 and is at the bottom of the vortex. A climatology, averaged over a 10-year period of PSCs, as a function of the month in Antarctica, is shown in Figure 3.

These shifts in altitude of the frequency of PSC occurrence are consistent with denitrification and dehydration of the vortex. The 1σ inter-annual variability in the frequency of PSC occurrence in the Antarctic stratosphere is ~0.2, from late August through September, at altitudes below 22 km. In relative terms, variability is greatest at the edge of the PSC probability envelope.

4. Similar data from the Arctic, centered near 0 to 40 degrees longitude, show the following:
 - December: maximum frequency is ~0.1, near 22 km
 - January: maximum frequency is ~0.25, near ~20 km
 - February: maximum frequency is ~0.25, near 19 km
 - March: not enough observations for analysis. The relative inter-annual variability in the monthly maximum frequency of occurrence in the Arctic is one percent. PSC occurrence is not easily predictable in the Arctic, unlike the case in the Antarctic.
5. It appears that in the Antarctic, temperatures must be colder as the winter progresses to get the same frequency of PSC occurrence. This is probably due to progressive dehydration and denitrification, which suppresses the thermodynamic temperature-threshold for particle formation. In the Arctic, the relationship between temperature and PSC occurrence in the winter months is statistically indistinguishable from month to month, and looks much like the Antarctic relationships in June and July, presumably due to a lack of denitrification and dehydration.

Lidar Observations: Information about stratospheric aerosol optical depth and vertical distribution has been obtained by lidar measurements. These include NASA Langley's ground-based ruby ($0.694 \mu\text{m}$) lidar, which has been in operation since 1974. This database provides the temporal variability of stratospheric aerosols, albeit at one location. Information about the phase of the particles has been derived from depolarization diversity data obtained by the Langley

differential lidar (of Dr. Browell) (Toon *et al.*, 1990) and single wavelength lidar (of Dr. McCormick) (Kent *et al.*, 1990). The information obtained from these lidar observations are discussed below:

1. An examination of the Langley, ground-based record shows that the stratospheric integrated lidar back-scatter at Langley is a reasonable surrogate for aerosol mass. Figure 4 shows the back-scatter history above Hampton, VA, obtained using lidar. The data also show that volcanic emissions control the aerosol mass and back-scatter with a small contribution from the continuous transport of gaseous sulfur compounds, such as COS, from the surface. There is some evidence for an increase in backscatter in the stratosphere from 1979 to 1990. It is very likely that the surface area falls more slowly than the integrated back-scatter (i.e., mass) following volcanic eruptions. The lidar data also show that decay in volcanic mass is not exponential, but rather that decay rate decreases with time.
2. Lidar observations have also been made from the DC-8 aircraft. Measurements on January 19, 1992, in the Arctic region, showed evidence of depolarization in a "streamer" at the top of the Mt. Pinatubo cloud, near 21 km, at the edge of the Arctic vortex (Browell *et al.*, 1993). The rest of the cloud showed no depolarization. The depolarization was quite large (approximately 10 percent), and is believed to be caused either by PSC particles or by frozen sulfate aerosols, with the latter possibility being more likely.
3. Comparison of the *in situ* data with satellite observations show that there are discrepancies at the bottom of the extinction profiles (below about 15 km). Therefore, care must be exercised in using such data.

In Situ Measurements

In situ measurements of particles can determine size distributions, composition, and number density of particles. Surface areas can then be derived from the size distributions. Such information is necessary to understand nucleation, condensation, coagulation, and sedimentation of atmospheric particles, and can be coupled with lidar measurements to validate satellite climatology of particle surface areas. Apart from the devices where the particles are collected on impactors or filter packs and brought back to the laboratory for analysis, most *in situ* measurements involve light-scattering methods. Light-scattering instruments include particle counters, nephelometers, polarimeters, back-scatter detectors, and photometers, and have been deployed at the surface and on balloons and aircraft. Composition information has been obtained via evaporation experiments (Rosen, 1971) or collection of particles for analysis. Analysis on the collected samples include elemental analysis (Sheridan *et al.*, 1992; Pueschel *et al.*, 1992) and, in the case of large particles collected on wire impactors, the shape of particles (Goodman *et al.*, 1989). Currently under development are instruments which measure light, scattered at two angles, in an attempt to directly measure index of refraction of particles. Up to now, refractive indices have been inferred from comparisons of *in situ*, size-distribution measurements with lidar back-scatter observations (Hofmann *et al.*, 1983; Adriani *et al.*, 1992).

The minimum particle sizes measurable, by light-scattering techniques, is limited to $\sim 0.1 \mu\text{m}$ radius without disturbing the particle. If the particles are measured with more powerful illumination and, thus, disturbed, particles as small as $0.03 \mu\text{m}$ can be measured (Wilson *et al.*, 1993). Even smaller particles can be detected and counted using condensation nucleus (CN) counters (Rosen and Hofmann, 1977). Uncertainties in the measured number concentrations are determined by Poisson counting statistics and depend on the sampling rate; uncertainties increase as particle size increases, since number density of such particles are smaller. For example, for counting uncertainties ranging from 1 to 100 percent, for particles between 0.1 and $1.5 \mu\text{m}$ radius, the associated uncertainties in mass and surface area are ~ 30 to 100 percent (Deshler *et*

al., 1993). In addition to errors due to sampling only a small number of large particles, uncertainties arise due to a lack of information on the particles' shape and refractive index, which impact the size inferred of the particle, based on its scattering properties.

In situ measurements over the past couple of decades have shown that stratospheric aerosols above 20 km are largely modulated by volcanic activity (Hofmann, 1988), in agreement with the satellite measurements. The SO₂ injected into the stratosphere by volcanic activity is transformed into H₂SO₄ via gas-phase oxidation processes. The H₂SO₄ then either condenses onto pre-existing particles or forms new particles through homogeneous and heteromolecular nucleation (Turco *et al.*, 1982). New particles are typically observed one to two months after a volcanic eruption (Hofmann and Rosen, 1982; Wilson *et al.*, 1983), consistent with theory. The number of condensation nuclei then decay rapidly (one to two months) due to coagulation and dilution (Deshler *et al.*, 1992a). For periods of more than a year, following volcanic eruptions, the number density of large particles and surface areas remain elevated by factors of 10 to 100, compared to quiescent periods. Example size distributions of aerosol, from volcanically-quiescent and volcanically-perturbed periods, are shown in Figure 5. The volcanically-perturbed periods are at 1.0, 2.0, and 2.7 years following the eruption of Mt. Pinatubo in June 1991. The evolution of the vertical distribution of surface area density during this same period is shown in Figure 6. The volcanic aerosol loading decays with an approximate time constant of three to five years for number density. The time constant is different for surface area and mass. To a first approximation, the quantity of interest is surface area; however, it is not clear that surface area decays exponentially or that background levels are reached between volcanic injections. The stratospheric sulfate aerosol surface areas, inferred from *in situ* measurements, can be coupled with lidar measurements to infer aerosol surface area, based on measurements of back scatter and, thus, obtain a more continuous record of stratospheric aerosol surface area (Jäger and Hofmann, 1991). This technique depends on knowledge of the particle index of refraction. Fortunately, this is reasonably well known for middle latitudes (Russell and Hamill, 1984), although discrepancies have been observed in polar regions (Deshler *et al.*, 1992b).

It has been suggested that the background level of the sulfate aerosols can be reconciled with the input of sulfur into the stratosphere in the form of carbonyl sulfide, which appears to have mostly a natural tropospheric origin (Crutzen, 1976; Toon *et al.*, 1979). However, recently there has been some suggestion that the background level of sulfate aerosol in the stratosphere is increasing (Hofmann, 1990). This conclusion needs to be examined further; unfortunately, large frequent volcanic eruptions during the last two decades have limited the time available for the stratosphere to cleanse itself of volcanic particles and, hence, enable quantification of "background" conditions.

Since the discovery of ozone depletion in 1985, there have been significant efforts directed at particles in the polar regions using *in situ* observations from balloons and aircraft. In general, in the Antarctic, PSCs have been observed when temperatures were below the equilibrium temperatures for nitric acid trihydrate (NAT), or below the frost point for the vapor contents measured or expected (Fahey *et al.*, 1989; Hofmann and Deshler, 1991; Gobbi *et al.*, 1991). These temperatures coincide with supersaturations, with respect to NAT, of near 1.0. The size distributions of PSC particles are usually found to contain two modes, one with median radii near 0.2 μm ; the other, near 2.0 μm (Hofmann and Deshler, 1991; Deshler *et al.*, 1994). Recent comparisons between lidar and *in situ* measurements in the Antarctic suggest two different refractive indices for particles in PSCs, at temperatures consistent with NAT, suggesting the existence of two different forms of NAT (Adriani *et al.*, 1994). This conclusion is consistent with earlier observations in Arctic PSCs, which showed two distinct lidar signatures from PSCs at temperatures near the NAT existence temperature (Toon *et al.*, 1990).

There is some evidence in the northern polar regions for PSC formation in the Arctic at NAT supersaturations of ~ 1 (Dye *et al.*, 1990; Hofmann *et al.*, 1990); however, the main onset of

PSCs appears to be at supersaturations of ~ 10 (Rosen *et al.*, 1989; Hofmann *et al.*, 1990; and Dye *et al.*, 1992). This is in contrast to the Antarctic where supersaturations for PSC observations were close to the thermodynamic limit of 1 (Fahey *et al.*, 1989). This difference may be indicative of some fundamental difference in the PSC nucleation process or in the nature of the sulfate aerosols at the core of PSCs, but most likely it reflects differences in the temperature history of the particles or their age. Observations of PSCs in the Antarctic are all in the late winter, which is a major deficiency in our observational database. Sulfate aerosols may be frozen in this season, perhaps providing less of a nucleation barrier to PSC formation. This distinction, however, may not be important. It has been suggested that sulfate aerosols may remain liquid down to 189 K and that they can swell due to the uptake of nitric acid and water to make a ternary solution. Such a hypothesis is consistent with some observations (T. Peter, this meeting). If correct, this suggests a large role for activation of chlorine and removal of N_2O_5 on liquid aerosols (Molina *et al.*, 1993).

In light of new laboratory measurements of sulfuric acid/nitric acid/water physical chemistry, theories of PSC formation are changing. The conventional theory is that stratospheric aerosol deliquesces down to 195 K – the nominal NAT threshold temperature (Steele and Hamill, 1981; Hanson and Mauersberger, 1988) – and then sulfuric acid freezes, NAT condenses on the frozen particles, and ice condensation follows. Example size distributions from measurements in Antarctica (Spring 1992), at different temperatures in this progression, are shown in Figure 7. Vertical profiles of surface-area concentrations for the Antarctic measurements are shown in Figure 8. As discussed in the next section and indicated above, it has also been suggested that PSC particles may grow as a ternary nitric acid/sulfuric acid/water solution. If true, freezing of sulfate aerosols is not needed for PSC formation. The phase of stratospheric particles, at and below 195 K, has not been measured directly and this uncertainty impacts on the refractive index of the particle and the consequent uncertainties in calculated surface areas. Particle composition information, or simultaneous particle measurements with measurements of the relevant constituent species, would be helpful here (Schlager *et al.*, 1990; Kawa *et al.*, 1992); however, collecting such information has been difficult. Efforts to expand these measurements and to measure particle index of refraction *in situ* are in progress.

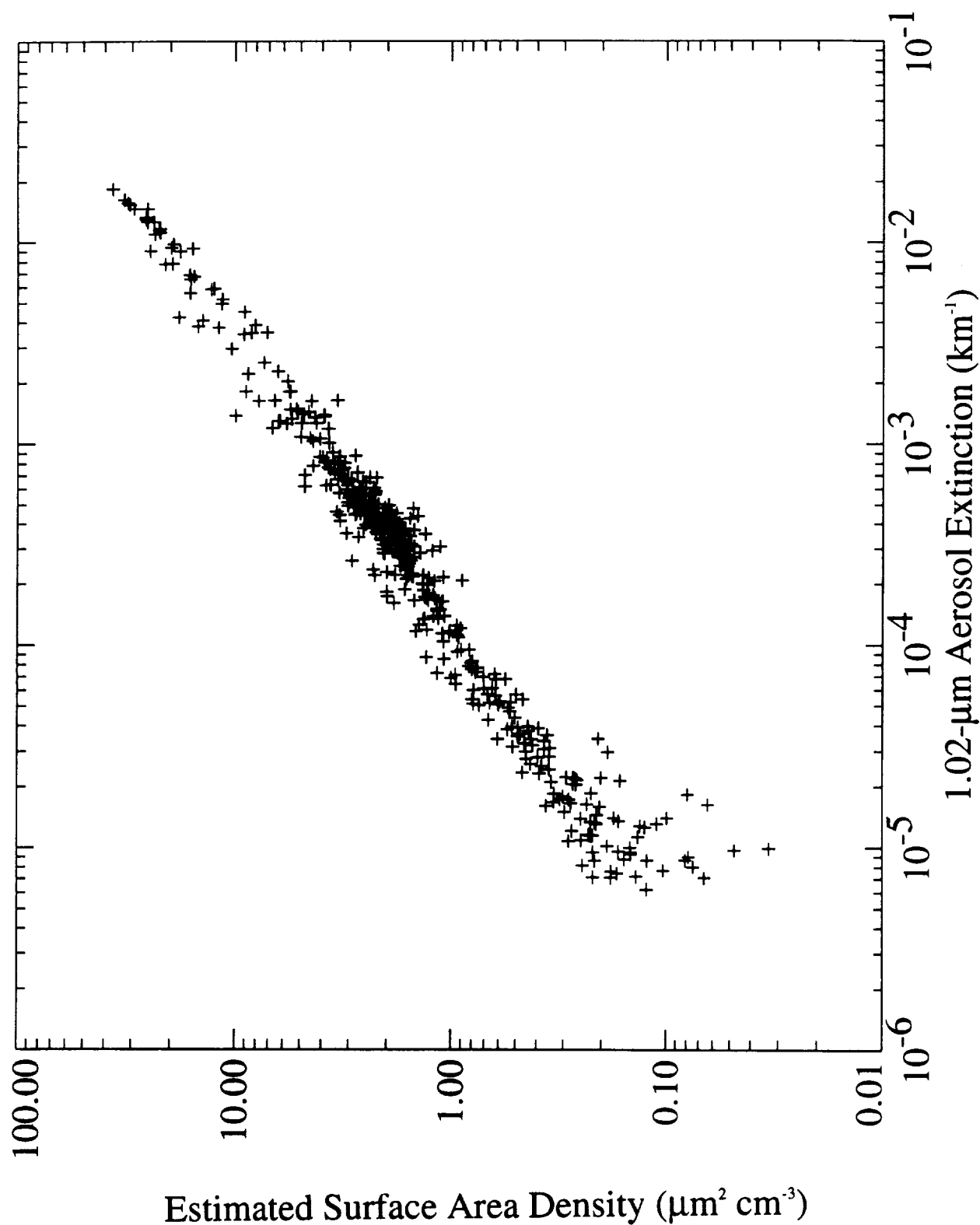


Figure 2. Relationship between aerosol surface area density (estimated from principal component analysis of multi-wavelength extinction data) and SAGE II 1.02- μm aerosol extinction.

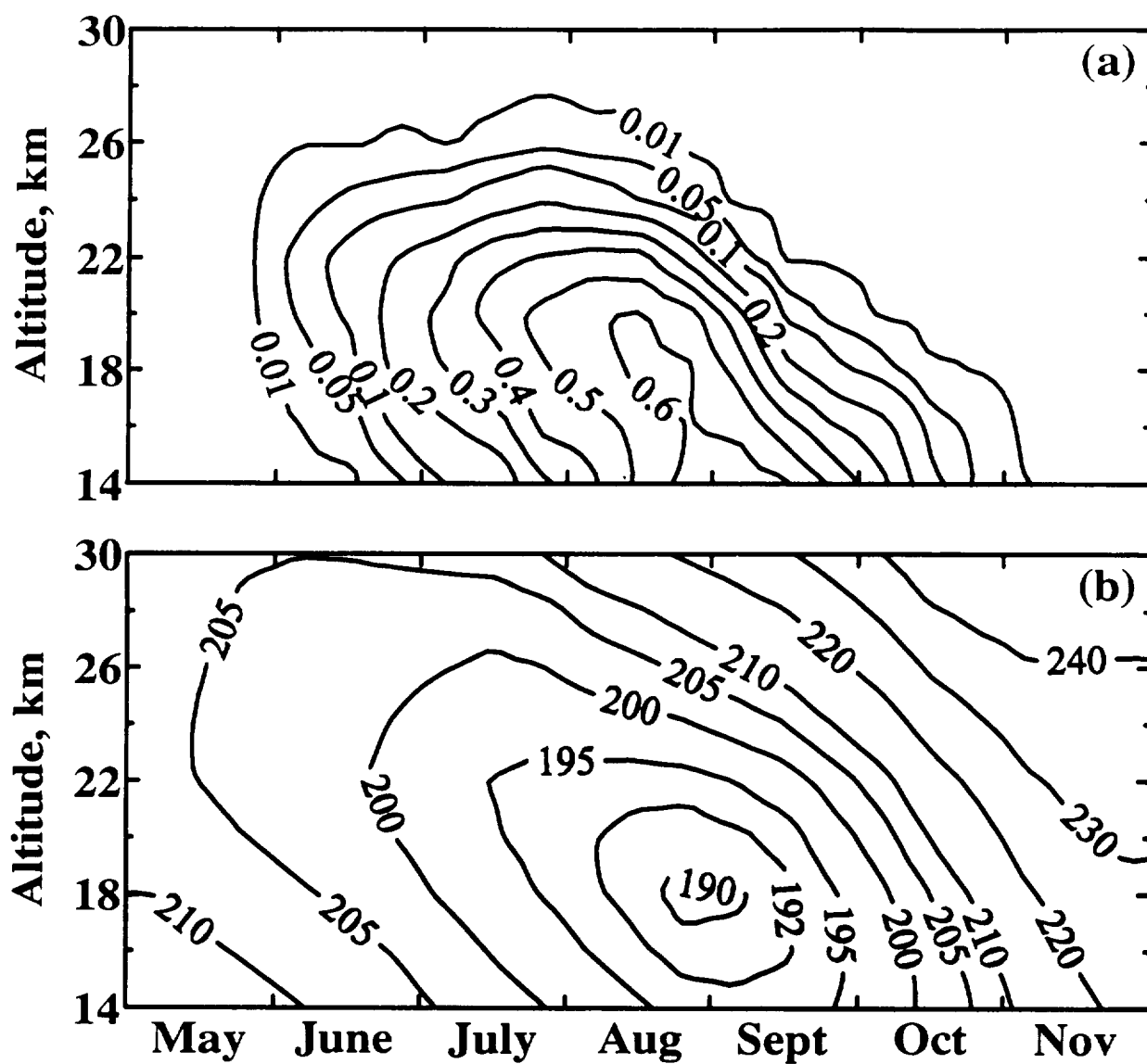


Figure 3. Zonally averaged (a) PSC sighting probabilities, and (b) NOAA temperatures for the Antarctic based on SAM II observations from 1979-1989 (Poole and Pitts, 1994).

STRATOSPHERIC INTEGRATED BACKSCATTER Aerosol Lidar Measurements at LaRC (37°N, 76°W)

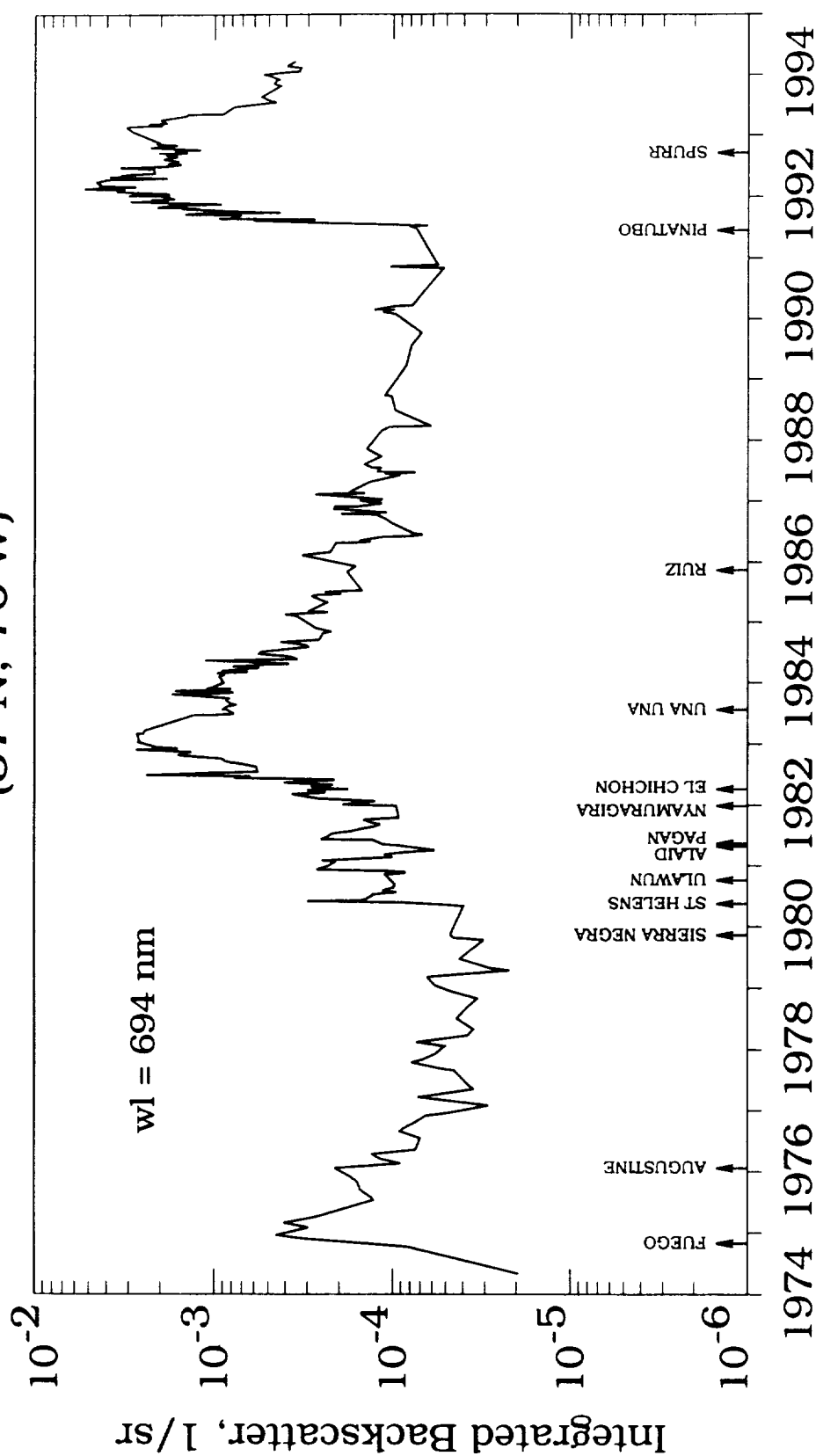


Figure 4. Long-term record of integrated stratospheric aerosol backscatter (from the tropopause to 30 km), obtained at NASA Langley Center (37°N, 76°W). Major volcanic eruptions are noted by arrows on the abscissa. (From Smithsonian Institution *Global Volcanism Network Bulletin*, 19, 11, 1994.)

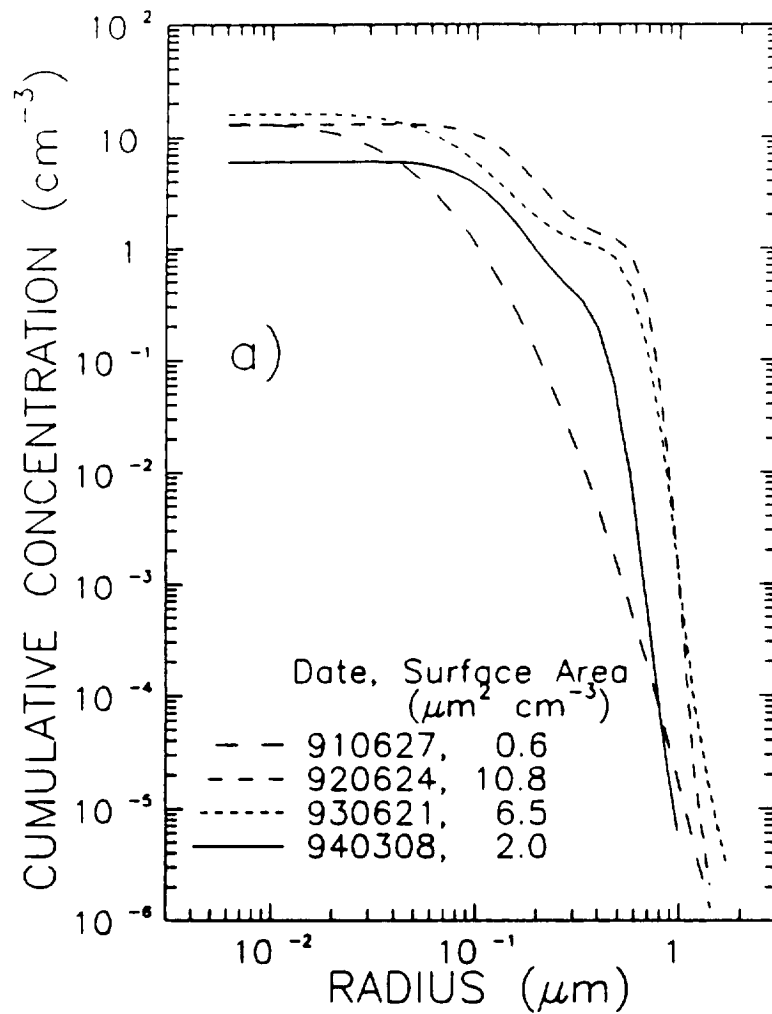


Figure 5. Example size distributions at 18 km at Laramie, Wyoming (41°N), during the volcanically-quiet period prior to the eruption of Mt. Pinatubo, and at 1.0, 2.0, 2.7 years following the eruption.

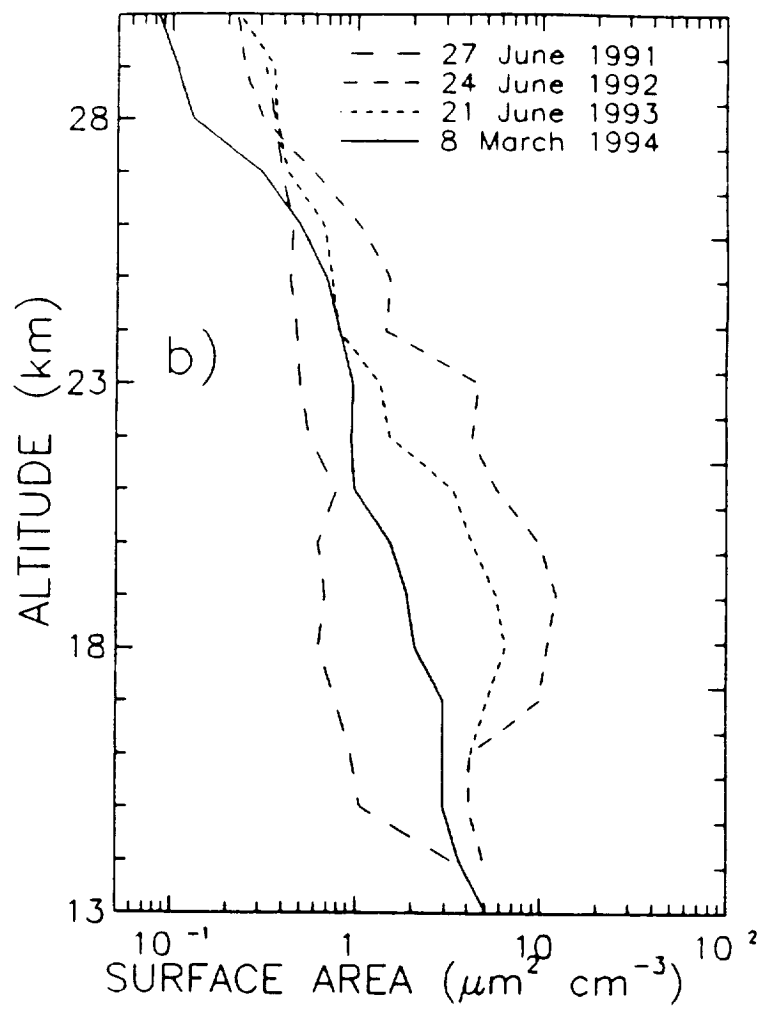


Figure 6. Vertical profiles of surface area density during the volcanically-quiet period prior to the eruption of Mt. Pinatubo, and at 1.0, 2.0, 2.7 years following the eruption.

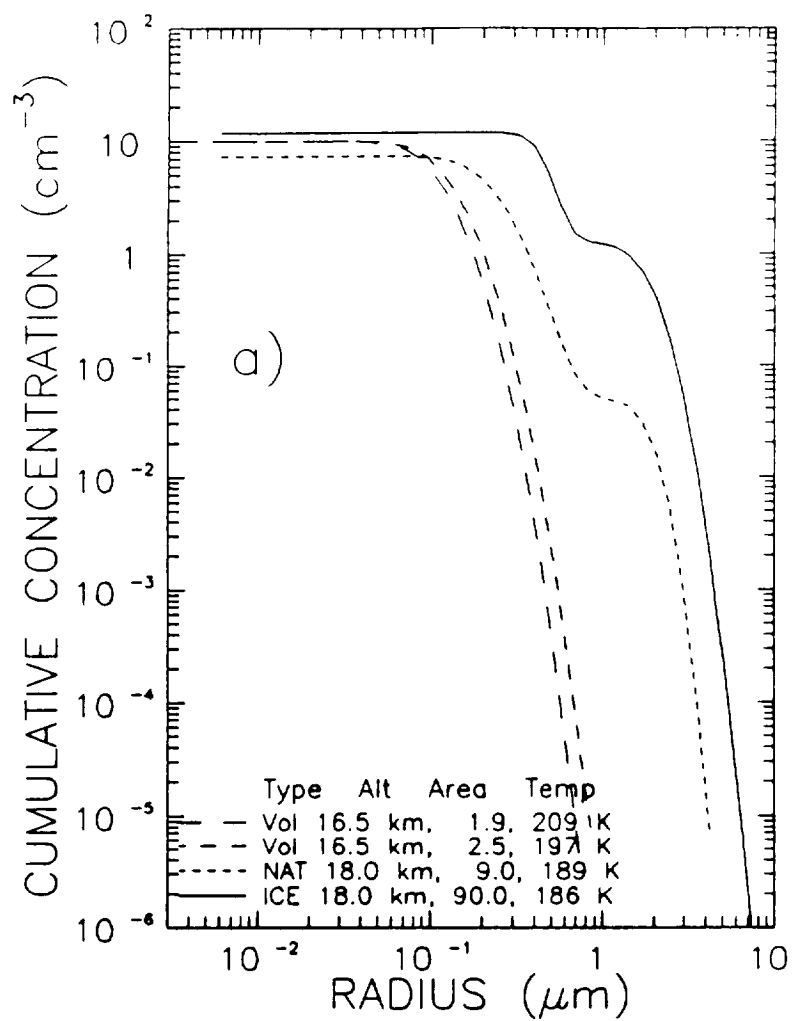


Figure 7. Example size distributions from Antarctic *in situ* aerosol measurements at McMurdo Station (78°S). The measurements were collected August - October 1992, the first spring after Mt. Pinatubo aerosol had been incorporated into the Antarctic polar vortex.

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LABORATORY STUDIES OF HETEROGENEOUS PROCESSES: PARTICLE FORMATION AND CHEMICAL REACTIONS

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Laboratory studies of the conditions for the formation of particles, the composition of particles, and the chemical reactions involving these particles are one of the cornerstones of atmospheric chemistry research. It is fair to say that without information on the thermodynamics, spectroscopy, and chemical reactivity of particles, the current understanding of stratospheric ozone would not be possible.

In this session, the current state of understanding of various aspects of heterogeneous chemistry, as studied by laboratory measurements, were discussed. They generally fall into two categories: the microphysics of when, where, what kind of, and how fast particles can be formed in the atmosphere; and the rates of various heterogeneous reactions in/on these particles. There are two general classes of particles in the stratosphere: PSC particles, which are confined mostly to the polar stratosphere during winter and spring; and stratospheric sulfate aerosols (SSAs), which are ubiquitous in the lower stratosphere. There are regions where they overlap in space and time. However, because the PSCs are (believed to be) solids and, in general, SSAs are liquids, the nature and rates of chemical processes will be different. However, to anticipate one of the findings of this workshop, it should be kept in mind that in the areas where there is a transition from SSA to PSC processing, the distinction between these two types of particles is absent! Yet, for ease of presentation and coordination of talks, this distinction was made here.

Discussions during this session centered around three questions:

1. Why do we believe that laboratory results are applicable to the atmosphere?
2. Which processes need refinements, verification, and/or further study?
3. What is "unknown" at the present time?

Investigations of Processes Relevant to Stratospheric PSC Formation

Workshop presentations and discussions showed that substantial progress has been made in understanding some crucial processes in measuring the necessary parameter for PSC formation: phase diagrams and solubilities have been measured; metastable hydrates have been identified and partially characterized; and other relevant parameters, for binary and ternary mixtures, have been determined. An important question was raised during the workshop discussion: Is it essential to simulate atmospheric aerosol particles in the laboratory to make laboratory studies useful and applicable to the stratosphere? The answer is "no!" Such a simulation does not necessarily improve our understanding of the basic processes and, hence, helps application to different conditions. In addition, aerosols under stratospheric conditions of size, composition, time scales, temperatures, and gas surrounding composition are improbable to obtain in the near future. Expending all our efforts on such a route is not the most useful approach. Goals of laboratory studies, on the other hand, should be to investigate processes on macroscopic and microscopic (molecular) scales, on surrogate surfaces, under well-controlled conditions, to probe aspects (such as solubilities, phase transition, reaction probabilities) that are relevant to PSC and

SSA processes in the atmosphere. Laboratory studies are guided by a "working model" which is assumed to represent atmospheric processes. Actual atmospheric measurements will provide verification of, and input to, refinements in laboratory studies. The statement above does not preclude, *per se*, the generation of aerosol particles in a laboratory environment and the probing of specific processes. Caution should always be exercised, however, to declare such experiments "stratospheric simulations." An additional benefit of laboratory investigations is the support they provide for the development of microphysical models.

The particles which provide the surface for heterogeneous reactions in the stratosphere are crystalline or amorphous solids, or supercooled liquid sulfuric acid droplets. Anticipating one of the findings of the workshop, the supercooled sulfuric acid droplets may also contain large amounts of HNO_3 . The solids have the bulk composition of ice or a hydrate of nitric acid. To predict what types of particles can be present (i.e., thermodynamically feasible) in the atmosphere under given conditions of temperature, water vapor pressure, and the mole fraction of nitric or sulfuric acids, the phase diagrams of these systems are needed. Even though the binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system has been studied for a long time (Gable *et al.*, 1950; Steele and Hamill, 1981), the other systems have been studied carefully only recently. There has been a great deal of progress in identifying various phases that can be produced. Ternary systems consisting of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HNO}_3$ and $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HCl}$ have also been recently studied (Zhang *et al.*, 1993). These data provide information on particle formation under equilibrium (i.e., thermodynamic) conditions in the stratosphere. Of course, the actual formation conditions may be different in the atmosphere because of kinetic constraints and a significant degree of supersaturation may be required for the formation of particles, as suggested by observations discussed in the section on climatology.

The efficiencies of various reactions change with the bulk, as well as with the surface composition of the particles. The composition of these surfaces is often assumed to be the same as that of the bulk; however, this may not be the case. There can be differences in both composition and structure. Such differences may be important for particle growth and for determining rates of reactions. One such example of gross changes in surface characteristics with changes in the vapor pressure of the constituents is the variation of the uptake coefficients for the $\text{ClONO}_2 + \text{HCl}$ reaction which changes with relative humidity (Hanson and Ravishankara, 1993; Abbatt and Molina, 1992; Zhang *et al.*, 1994). The increase in reactivity with relative humidity suggests changes in the surface composition. The differences between the composition and structure of the surface and of the bulk needs to be better understood.

The nucleation of a metastable phase may be kinetically faster than that of the stable phases at that temperature (Worsnop *et al.*, 1993). Such differences can play crucial roles in determining the nucleation and growth of particles. Significant advances in this area have been accomplished; yet, it is evident that we are not in a position to accurately predict when Type I PSCs are formed.

Summarized below are the possible "mechanisms" for PSC formation processes, which have been supported by recent results of laboratory studies. It became clear during the workshop that a better understanding of PSC formation and occurrence can be achieved when actually considering two processes:

1. *The process of initial cool-down at the onset of polar winter. Laboratory studies have concentrated on this period.*
2. *Processing and recycling of PSCs, as the air mass is warmed and cooled over periods of months.*

These two aspects are discussed below.

1. Sulfate aerosols are liquid above approximately 200 K. Laboratory studies have clearly shown that, as temperature decreases, aerosol particles will take on water and HNO₃, forming ternary solutions while becoming diluted in H₂SO₄ and enriched in HNO₃. The phase diagram of the ternary mixtures of H₂SO₄/HNO₃/H₂O is shown in Figure 9 (Molina *et al.*, 1993). To a lesser extent, HCl will also be dissolved. The latter process is considerably less well quantified and needs refinement and/or verification.

Cooling of SSAs will lead to supersaturation in HNO₃ with respect to NAT equilibrium conditions, as the liquid reaches approximately 194 K. The phase diagram of the binary H₂O/HNO₃ mixtures is shown in Figure 10 (Worsnop *et al.*, 1993). Laboratory experiments suggest that nitric acid dihydrate (NAD) may nucleate before NAT. If this is true, NAT formation must have a kinetic barrier, and the temperatures at which PSCs form may be lower than predicted by thermodynamics. It should be noted, however, that in the Antarctic winter/spring stratosphere, temperatures for the appearance of PSCs (presumably NAT) are consistent with the thermodynamics for NAT. This may suggest that, at least, some SSAs are frozen in winter in Antarctica.

The fate of the aerosols below this temperature is less certain. One set of laboratory studies has been used to conclude that NAT will crystallize out of the solution followed by freezing of sulfuric acid tetrahydrate (SAT) (Molina *et al.*, 1993). This conclusion needs to be checked.

In another scenario, freezing of the aerosol may not occur until temperatures drop below 190 K, or even below the frost point (Middlebrook *et al.*, 1993). Metastable nitric acid hydrates may also form, such as NAD, nitric acid monohydrate (NAM), or nitric acid pentahydrate (NAP), which may eventually change into NAT, the most stable hydrate under stratospheric condition (Worsnop *et al.*, 1993; Marti and Mauersberger, 1993, 1994). Freezing of the sulfate aerosol will occur at some undetermined temperature below 190 K. As in the SAT formation possibility, the cooling of aerosols below 190 K needs verification.

2. PSC Recycling. Temperature fluctuations, which are very common in the Arctic stratosphere, may change the phase, composition, and surface area of cloud particles.

As temperatures increase, NAT particles will evaporate (according to the phase diagram) near or above 196 K. SAT particles will remain frozen or may otherwise form as higher temperatures are reached (Iraci *et al.*, 1994). Finally, at temperatures around 210-215 K, the frozen aerosols will melt (Middlebrook *et al.*, 1993; Zhang *et al.*, 1993). It should be recognized that the warming process generally proceeds along thermodynamically-predictable pathways, represented by the phase diagram.

Subsequent cooling of SSAs (assuming SAT particles remain frozen), may lead to nucleation on frozen particles, perhaps under near-equilibrium conditions. Then, NAT particles may readily form near 196 K, without much supersaturation. Currently, it is not known if metastable states, such as NAD or NAP, could also be formed.

Investigation of Reactions in/on Stratospheric Particles

It is now recognized that heterogeneous chemistry on PSCs and in SSAs can have a profound influence on global ozone. Five heterogeneous reactions, which play important roles in ozone depletion by re-partitioning ClO_x and NO_x in the stratosphere, have been identified:





Reactions (2-5) all convert inert chlorine (ClONO_2 , HCl) into photochemically active forms (HOCl , Cl_2 , ClNO_2). Upon photolysis, these molecules release Cl (or ClO) that participate in catalytic ozone destruction cycles. Reactions (1-3 and 5) all result in nitric acid formation. This leads to "denoxification," or the temporary lowering of NO_x ($= \text{NO} + \text{NO}_2$), by conversion to HNO_3 . Permanent removal of NO_y ($= \text{NO}_x + \text{HNO}_3 + \text{N}_2\text{O}_5 + \text{ClONO}_2$), or "denitrification," can occur if particulate HNO_3 falls out of the stratosphere by sedimentation. A result of denoxification or denitrification is that less NO_x is available for sequestering active chlorine back into inactive forms through, for example, reaction (6):



Therefore, it can be seen that even heterogeneous reactions involving only odd nitrogen (i.e., reaction 1) can indirectly affect ClO_x .

Experimental measurements are summarized below for heterogeneous reaction rates on laboratory surfaces that model stratospheric particles.

Heterogeneous Reactions in/on Sulfuric Acid: SSAs are composed of supercooled solutions of sulfuric acid in water. The acid concentration of aerosols is dictated by temperature and water vapor partial pressure (Steele and Hamill, 1981). If water vapor partial pressure is greater than the vapor pressure of water over the sulfuric acid, the droplets will absorb water to maintain equilibrium. For stratospheric temperatures in the range 205 to 240 K, the expected composition of the aerosol is 60 to 80 weight percent (wt.%) H_2SO_4 . Figure 11 shows the freezing envelope for $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions, as well as the composition of SSAs for a fixed water vapor pressure (of 2×10^{-4} Torr) in the atmosphere. When this mixture remains supercooled, the wt.% of the sulfuric acid can be calculated from this data. These supercooled aerosols are distributed globally, and dramatically increase in abundance after major volcanic eruptions such as El Chichon (1982) and Mt. Pinatubo (1991) (See previous section on climatology). For temperatures lower than 205 K, the sulfuric acid aerosols can become quite dilute, near 40 wt.% H_2SO_4 at 190 K for 2×10^{-4} Torr H_2O , if they remain a liquid. For temperatures this low, the sulfuric acid aerosols may eventually freeze. Once frozen, the aerosols are expected to stay frozen until a temperature raises to 210-215 K (Middlebrook *et al.*, 1993; Zhang *et al.*, 1993). Thus, heterogeneous chemistry on sulfuric acid aerosols must be considered for concentrated H_2SO_4 solutions, dilute solutions, and frozen solids.

Laboratory studies over the last several years have shown that hydrolysis of N_2O_5 (reaction 1) occurs rapidly ($\gamma \sim 0.1$) for all compositions of supercooled sulfuric acid, with very little temperature dependence (Tolbert, 1993) (Figure 12). Because this reaction is so rapid on all compositions of aerosol, the rate of conversion of N_2O_5 to HNO_3 is essentially limited by the formation of N_2O_5 , rather than by reaction (1), at altitudes below ~ 24 km for background aerosol loading conditions. In other words, the conversion rate is "saturated" with respect to heterogeneous processing (Mills *et al.*, 1993; Prather, 1992). Under volcanic conditions, this "saturation" could extend much higher into the stratosphere. Thus, an increase in aerosol mass in the lower stratosphere is not likely to enhance the overall conversion of N_2O_5 to HNO_3 , or to increase the ratio of HNO_3 to NO_x . In contrast, the rate of ClONO_2 hydrolysis (reaction 2) increases very rapidly as the aerosol becomes dilute (Figure 13). In the stratosphere, where the

partial pressure of H₂O is not varying rapidly, this change in reactivity with wt.% (i.e., composition) manifests itself as a strong temperature dependence, with an increasing reaction rate at low temperatures where the aerosols are most dilute. Because reaction (2) is relatively slow in non-polar regions, compared to the ClONO₂ formation step, increases in sulfuric acid loading in the stratosphere will lead to corresponding increases in the conversion of ClONO₂ to HOCl (Solomon *et al.*, 1993; WMO, 1992).

A framework for inclusion of liquid sulfuric acid chemistry into models of the stratosphere has recently been provided by Hanson *et al.* (1994). They define a "diffuso-reactive" length, $l = (D/k)^{1/2}$, to characterize how much of the aerosol droplet participates in the heterogeneous chemistry. Here, D (cm² s⁻¹) is the condensed phase diffusion coefficient and k (s⁻¹) is the pseudo, first-order rate constant for the condensed phase reaction. When l is much less than the aerosol radius, the reaction is confined to the surface and the aerosol surface area controls the overall reaction rate. When l is greater than or equal to the aerosol radius, the entire aerosol particle participates in the reaction. Here, the volume of aerosol is the important factor for determining the overall reaction rate. Hanson *et al.* (1994) find that reaction (1) is surface controlled and, thus, γ measured in the laboratory over bulk substrates can be directly applied to the atmosphere. In contrast, reaction (2) may take place well within the droplet and, thus, corrections must be applied to γ s measured in the laboratory on bulk substrates for use in atmospheric models.

To accurately include the bimolecular reactions (3-5) in liquid aerosols under a variety of conditions, the Hanson *et al.* (1994) model needs, as input, the solubility of HCl in sulfuric acid, H^* ; the diffusion coefficients, D ; and the rate coefficients, k . These parameters are currently not well established. Values for the HCl solubility in 50 wt.% H₂SO₄, at 195 K, vary by almost an order of magnitude (Zhang *et al.*, 1993; Luo *et al.*, 1994; Williams and Golden, 1993; Hanson and Ravishankara, 1993a) (Figure 14). No directly measured diffusion coefficients exist. The separate measurements of $H\sqrt{D}$ and H for HCl under one set of conditions has provided some information on D . The theoretical approach of the Mainz group to calculate the diffusion coefficients appears to be accurate and well founded (Peter *et al.*, heterogeneous chemistry workshop). New viscosity data by Williams (private communication, 1994) provide a stronger basis for calculated diffusion coefficients. For the most part, the second order rate constants for reactions (1-5) in liquids have not been measured. These values are needed as a function of temperature and wt.% H₂SO₄. In general terms, reactions involving HCl appear to be limited by the availability of HCl in solution for reaction. Because the HCl solubility increases with decreasing temperature and decreasing H₂SO₄ concentration, reactions (3-5) should increase in importance for low stratospheric temperatures where the aerosols are most dilute.

At very low temperatures, possibly after the formation of PSCs, the sulfuric acid aerosols may remain frozen as sulfuric acid tetrahydrate (SAT) until the temperature rises above ~210-215 K. Although there are relatively few studies of heterogeneous reactions on frozen sulfate aerosols, some general conclusions can be drawn. Reaction (1), which is fast on all liquid sulfuric acid solutions, appears to be quite slow on frozen SAT even at high relative humidity (Hanson and Ravishankara, 1993a). Reaction (2) also appears to be slower on SAT than in liquid sulfuric acid, although there is a factor of ~5 difference in the measured values of γ on SAT at high relative humidity (Hanson and Ravishankara, 1993a; Zhang *et al.*, 1994). In contrast to the above, reaction (3) occurs readily on SAT surfaces at high relative humidity (Hanson and Ravishankara, 1993b; Zhang *et al.*, 1994). The rate of reaction (3) on SAT decreases as the relative humidity decreases, as shown in Figure 15, in a manner similar to that on NAT. Reactions (4) and (5) have not yet been studied on frozen sulfuric acid. Overall, it appears that the reactivity of frozen sulfuric acid is markedly different from that of liquid sulfuric acid. Thus, it is essential to have a thorough understanding of what controls the phase of the aerosols in the stratosphere. Additional laboratory and field data probing the phase of aerosols

are needed. Measurements of the optical properties of low temperature liquid and frozen sulfuric acid would aid in the field identification of these aerosols.

For liquid sulfuric acid aerosols expected under global conditions, recent work has shown that it may be necessary to consider more than the five heterogeneous reactions discussed above. Laboratory work indicates that molecules in the HO_x family may be taken up quite readily by sulfuric acid solutions. For example, recent studies have shown that OH and HO_2 (Hanson *et al.*, 1992), as well as CH_2O (Tolbert *et al.*, 1993), are all rapidly taken up by sulfuric acid solutions. For OH and HO_2 , the competing gas-phase reactions are so rapid that heterogeneous loss does not significantly perturb the budget, at least under "background" conditions. However, condensed phase reaction of these species in solution may impact other radical families. Also, uptake of HO_x reservoirs, such as CH_2O , may impact HO_x , NO_x , or ClO_x chemistry. Additional uptake and reactivity studies are needed to quantify the role of condensed phase HO_x chemistry in sulfate aerosols.

Another issue of concern is that there are very few measurements of heterogeneous reactivity on actual sub-micrometer-sized aerosols. Fried *et al.* (1994) recently measured the rate of reaction (1), as a function of temperature and wt.% H_2SO_4 , on sub-micron-sized aerosols. Overall, agreement between the measured rates on small aerosols and bulk samples is excellent. This gives us confidence that laboratory measurements of reactivity on bulk samples are relevant to the stratosphere. However, it should be remembered that one should not expect variations in reactive uptake with size for reaction (1). That is not the case for other reactions. Therefore, studies of other reactions on aerosols are needed to make sure that we can treat these reactions correctly in the atmosphere. In addition, it is not yet clear if laboratory measurements of microphysical processes, such as aerosol freezing, are similar on bulk versus microscopic samples. Additional aerosol studies on this topic are also needed.

In addition to the above, there are other uncertainties in our understanding of heterogeneous chemistry in/on sulfate aerosols. For example, we are unsure of the detailed chemical mechanism for these heterogeneous reactions. The area of condensed phase photochemistry in sulfate aerosols is almost completely unexplored. These topics are of fundamental interest, and delving into them may lead us to answer some of the questions that were raised, as well as to better enable us to predict the feasibility of reactions that have not yet been studied. However, such an understanding may be of secondary importance for the aircraft program.

Heterogeneous Processes on PSC Surfaces: The rates of heterogeneous reactions (1-5) on model PSC surfaces are summarized in Table 1 and 2, which are taken from Tolbert's recent review (Tolbert, 1993).

In general, all of these reactions are very rapid on ice surfaces, representative of Type II PSCs. On NAT surfaces, these reactions exhibit a very strong dependence on relative humidity. In the atmosphere, this translates into a strong dependence on temperature, with reactions occurring more rapidly at low temperatures where the relative humidity is larger. For reactions (3) and (4), the rate appears to increase by two orders of magnitude in going from " HNO_3 "-rich to " H_2O "-rich NAT (Abbatt and Molina, 1992a,b; Hanson and Ravishankara, 1993b; Tabazadeh and Turco, 1993). A very important finding in the last year is that the rate of reaction (3) on solid stratospheric particles appears to *only* depend on the relative humidity to first order. Thus, NAT, NAD, and SAT all exhibit the same reactivity (Hanson and Ravishankara, 1993b). This suggests that the composition of Type I PSCs might be somewhat less important than previously thought. Although the chemical reactivity appears only to depend on relative humidity, it is still important to identify whether particles are SAT or PSCs, because the available surface area from PSCs are much greater than those from SAT for fixed partial pressures of H_2O and HNO_3 .

Table 1. Reaction probabilities for reactions (1) and (2) on PSC surfaces

ClONO ₂			N ₂ O ₅		
Reference	Ice	'NAT'	Reference	Ice	'NAT'
<u>Values that may reflect surface saturation and/or melting</u>					
Molina <i>et al.</i> , 1987	(0.02)		Tolbert <i>et al.</i> , 1988	(>0.001)	
Tolbert <i>et al.</i> , 1987	(0.009)		Leu, 1988b	(0.028)	
Leu, 1988a	(0.06)		Quinlan <i>et al.</i> , 1990	(0.03)	(0.015)
<u>More recent measurements</u>					
Moore <i>et al.</i> , 1990		0.02a			
Leu <i>et al.</i> , 1991		0.001a			
Hanson and Ravishankara, 1991b	0.3	0.006	Hanson and Ravishankara, 1991b	0.024	0.0006
Abbatt and Molina, 1992a	>0.02	0.001-0.002a	Kenner <i>et al.</i> , 1992	0.01-0.02	

a. Values on "Water-rich" NAT. Values on "pure" NAT are considerably lower.

Table 2. Probabilities for reactions (3-5) involving HCl on PSC surfaces

Reference	Ice	NAT
<u>ClONO₂ + HCl</u>		
Molina <i>et al.</i>	0.05-0.1	
Leu <i>et al.</i> , 1988a	0.06-0.3	
Moore <i>et al.</i> , 1990		0.06-1.0
Leu <i>et al.</i> , 1991		0.1
Hanson and Ravishankara, 1991b	a	0.3
Hanson and Ravishankara, 1992	>0.3	>0.2
Abbatt and Molina, 1992a	>0.2	>0.2b
<u>N₂O₅ + HCl</u>		
Tolbert <i>et al.</i> , 1988	>0.003	
Leu, 1988b	0.05	
Hanson and Ravishankara, 1991b	a	0.0032
<u>HOCl + HCl</u>		
Hanson and Ravishankara, 1992	>0.3	0.1
Abbatt and Molina, 1992b	0.16-0.24	0.17b

Of the five reactions listed above, the least studied is reaction (5), involving N₂O₅ and HCl. This reaction could be important in activating chlorine where ClONO₂ is low. The dependence of reaction (5) on relative humidity has not been studied and merits investigation. Perhaps more troubling is that recent field observations suggest ClONO₂ abundance to be equal to or higher than that of HCl. Reaction (3) has not yet been thoroughly investigated in the low HCl limit. If

HCl is a less important chlorine reservoir than previously thought, reactions involving HCl need to be studied at lower HCl pressures. This also implies a larger role for reaction (2), when HCl levels are very low due to heterogeneous processing.

One of the main controversies surrounding heterogeneous chemistry on PSCs involves available surface area in laboratory ices. Laboratory data by Keyser and Leu (1993a,b) suggest that laboratory ice surfaces can be very porous, at least in their experiments. These authors propose correcting laboratory-measured reaction rates on bulk ice to account for the differences between internal surface area (due to porosity of ices) and external "geometrical" surface area (Keyser *et al.*, 1991). In contrast, Hanson and Ravishankara (1992) measure γ values that are relatively independent of film thickness, suggesting that their ice substrates are not extremely porous. This controversy should be resolved before we can assess the applicability of laboratory-measured γ values to actual PSCs. Note, however, that for large γ values, the correction for internal surface area is quite small (Keyser *et al.*, 1991). Thus, the question of porosity will not change the overall picture that reactions (1-4) are very rapid on ice and on NAT at high relative humidities. Also note that the morphology and even the surface area of actual PSCs is still loosely defined. Further, very few models actually compute the rate of heterogeneous processing on PSCs. The actual rate of processing on PSCs is not very important for polar, especially Antarctic, vortex chemistry. However, if one needs to explore the possibility of low levels of PSCs outside the vortices, it is necessary to quantify the rate of PSC processing. Computation of these rates are essential, if heterogeneous processing is in competition with photochemistry. In such a case, both the chemically active surface area and the absolute values of γ are needed.

In addition to reactions (1-5), there have recently been several studies of other heterogeneous reactions on PSC surfaces. Most of the reactions exhibit small reaction probabilities. However, recent work by Friedl *et al.* (private communication) shows a very large reaction probability for pernitric acid (PNA = HO_2NO_2) on ice surfaces ($\gamma = 0.15$). It is not known if adsorbed PNA on ice could react with other adsorbed species, or if adsorption takes place on NAT also. Additional studies of reactions of HO_x and NO_x reservoir species and other possible chlorine species, such as CH_3OCl on PSC surfaces, are needed to assess their importance.

As was the case for sulfate chemistry, there are also large uncertainties in the fundamental mechanism for heterogeneous reactions on Type I PSCs. Knowledge of the surface mechanisms might explain some of the observations, such as the strong dependence of γ on relative humidity. Such studies should be pursued.

Finally, there have been no studies to date of heterogeneous chemistry on actual micron or sub-micron-sized ice or $\text{HNO}_3/\text{H}_2\text{O}$ particles. Although the reactivity is expected to be similar on particles, versus thin films, this needs to be verified. Studies on actual aerosols may also help settle the controversy regarding the role of internal surface area. In addition, aerosol studies should yield insight into the nucleation and growth of Type I PSCs, as well as their chemical composition.

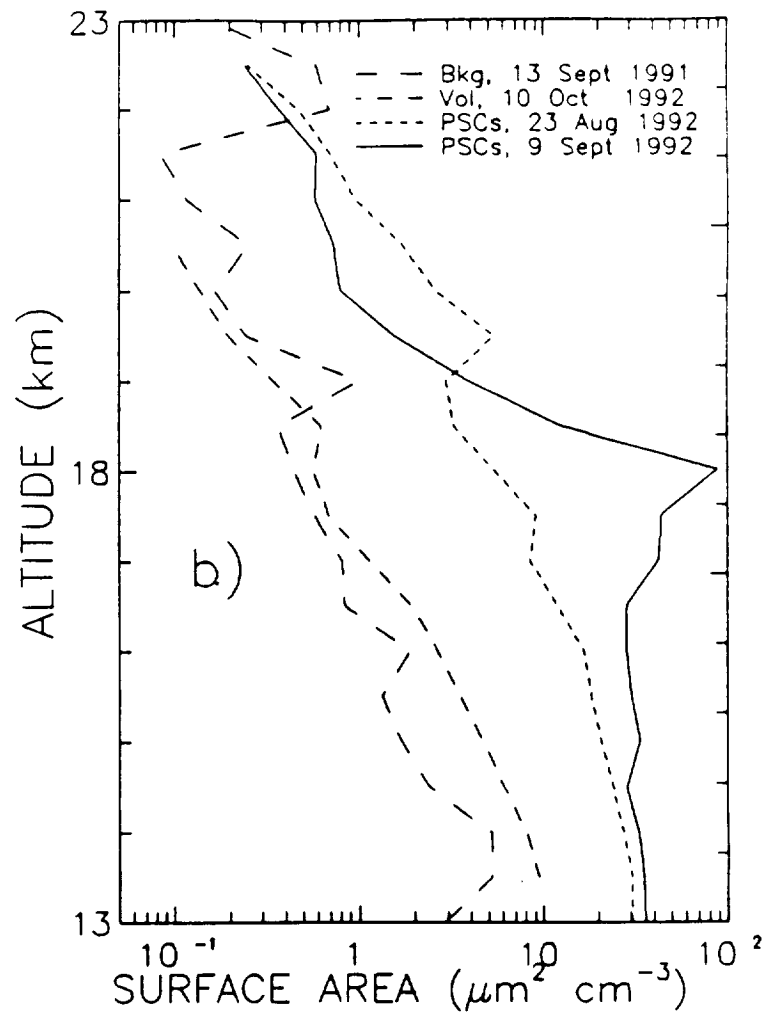


Figure 8. Vertical profiles of surface area density for different types of Antarctic stratospheric aerosol. The measurements were collected August - October 1992, the first spring after Mt. Pinatubo aerosol had been incorporated into the Antarctic polar vortex. The peak, at 18 km, coincides with an observation of a PSC ice cloud.

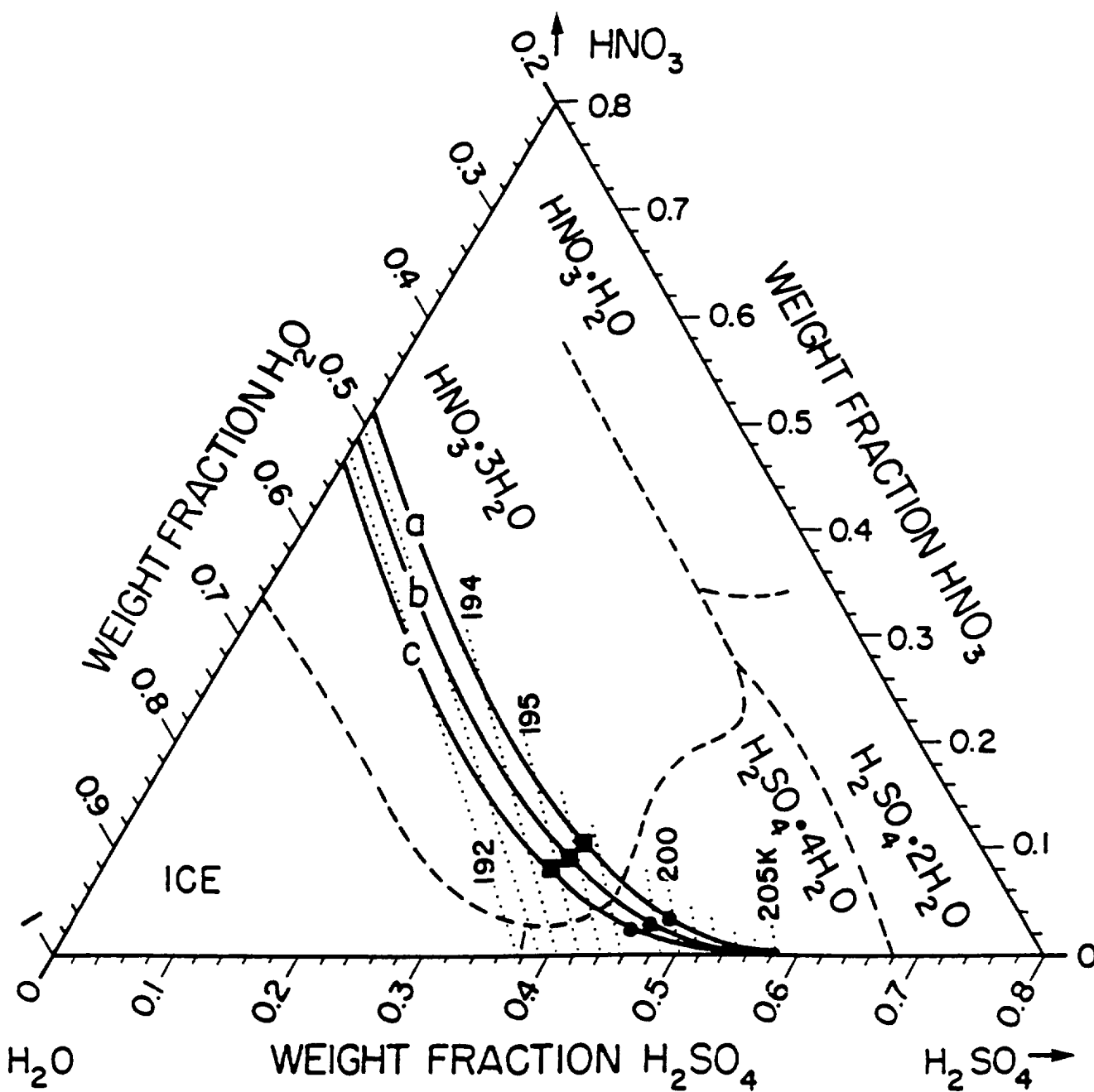


Figure 9. The phase diagram of the ternary $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ system from Molina's laboratory (Molina *et al.*, 1993).

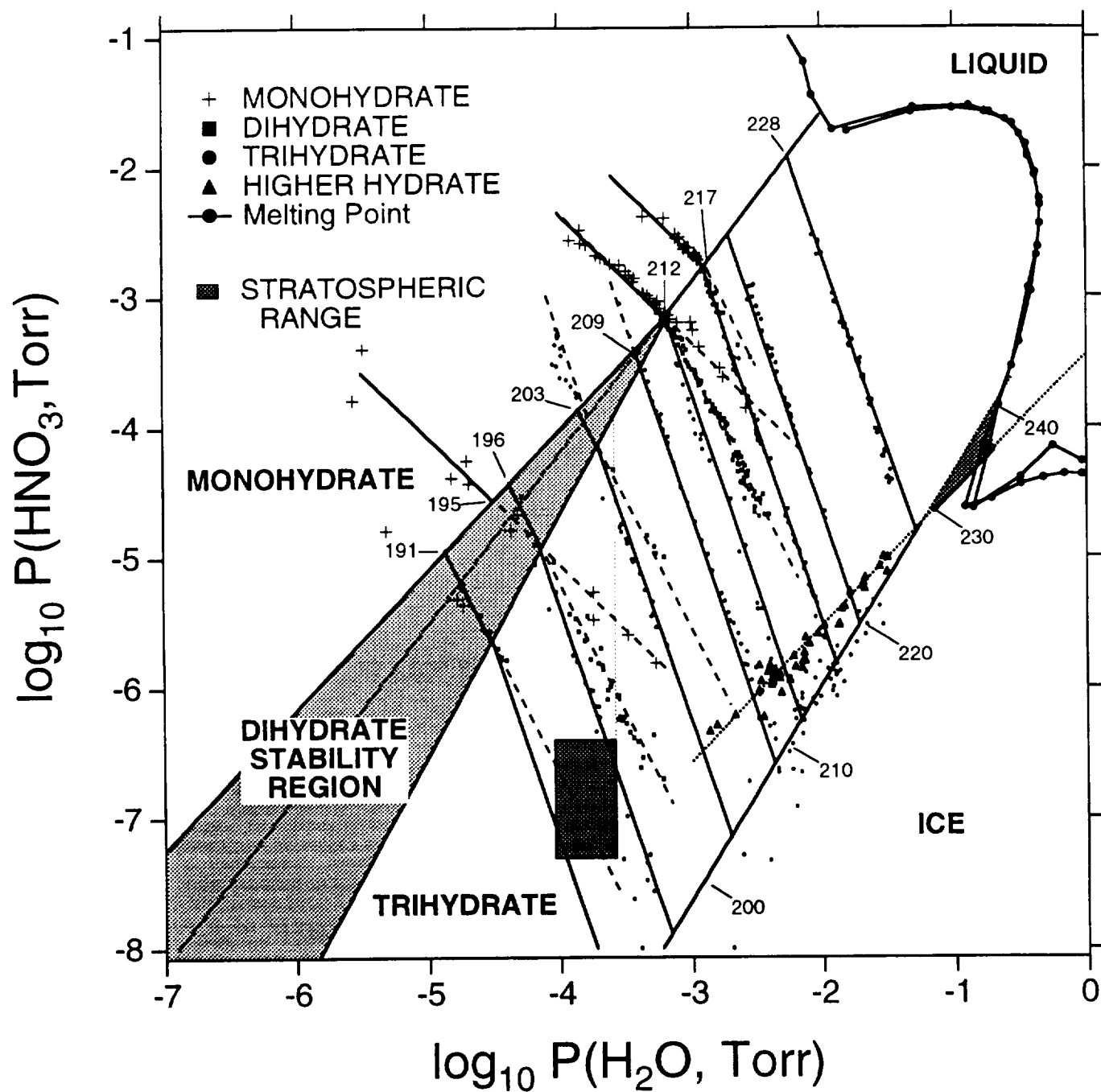
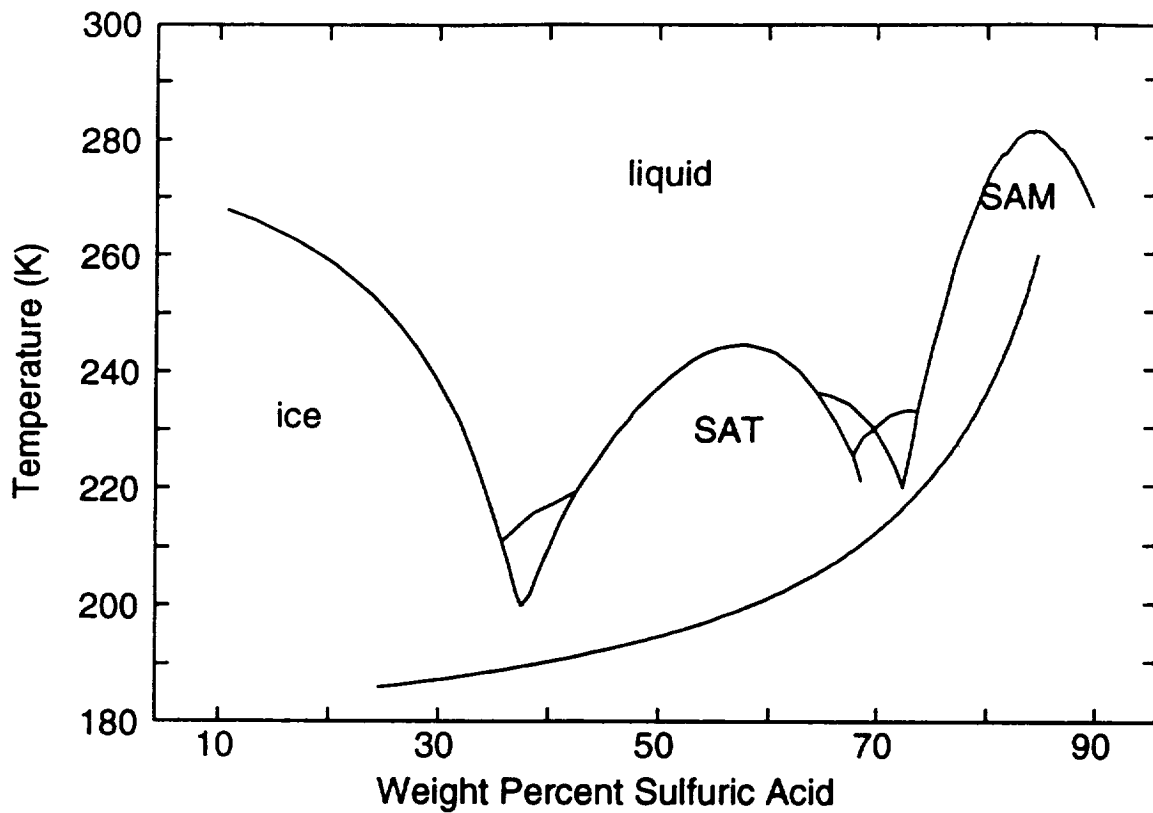


Figure 10. The phase diagram of the binary of $\text{HNO}_3/\text{H}_2\text{O}$ system from Aerodyne Research laboratory (Worsnop *et al.*, 1993).

Sulfuric Acid Phase Diagram

Dilution Curve for 2×10^{-4} Torr Water



Gable et al., 1950
Steele & Hamill, 1981

Figure 11. The melting point curve for H₂SO₄/H₂O system. The line inside the solid envelope is the composition of the supercooled sulfuric acid for 5 ppmv water vapor at 50 mbar. The data is from Gable *et al.* (1950) and Steele and Hamill (1981).

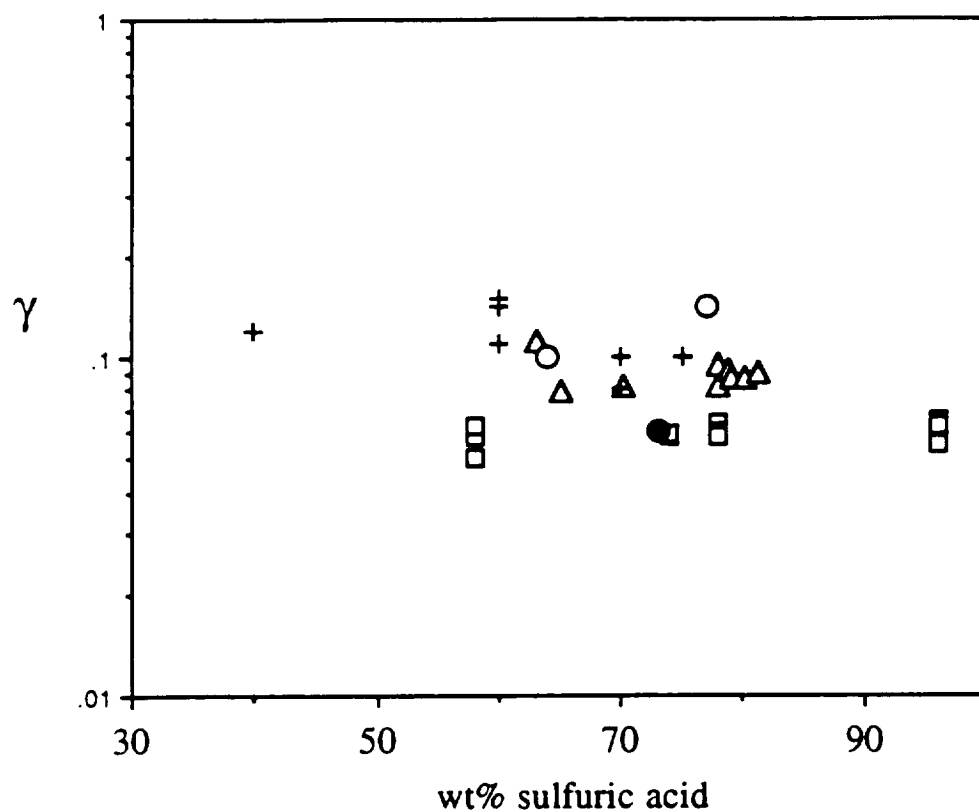


Figure 12. The reactive uptake coefficient for reaction (1) on sulfuric acid, as a function of wt.% sulfuric acid. (Pluses: 215-250 K, Hanson and Ravishankara [1991a]; triangles: 273 K, Fried *et al.* [1994]; squares: 220-300 K, Golden *et al.* [1992]; filled circles: 283 K, Van Doren *et al.* [1991]; open circles, 274-293 K, Mozurkewich and Calvert [1988]).

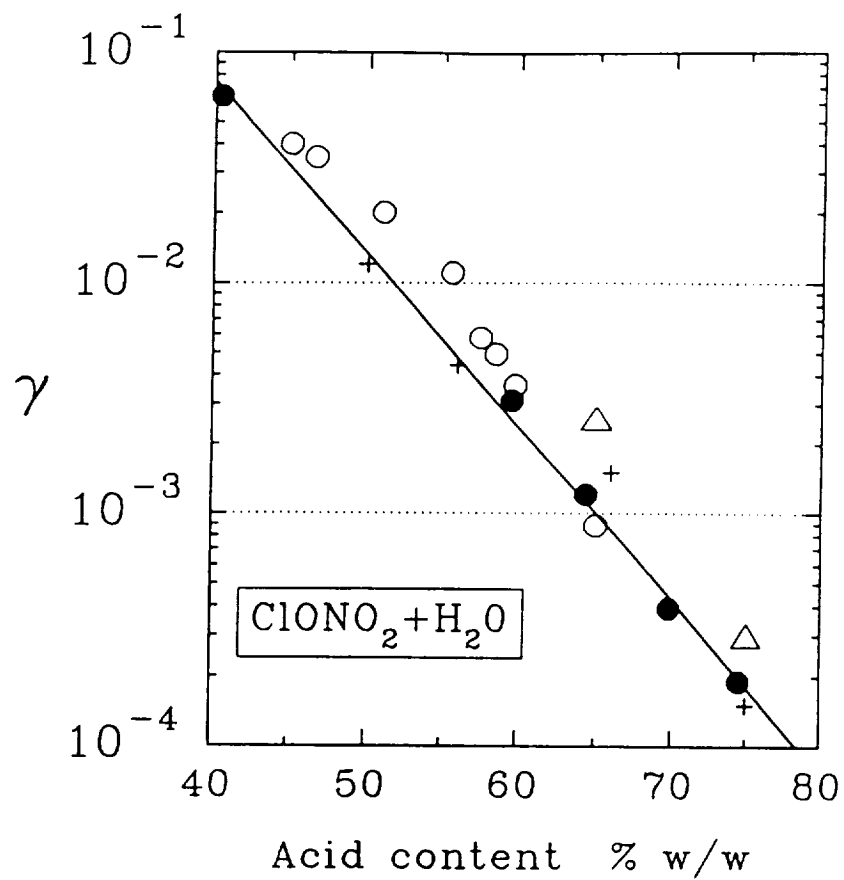


Figure 13. The reactive uptake coefficient for reaction (2) on sulfuric acid, as a function of wt.% sulfuric acid. Open circles are from Hanson and Ravishankara (1994); filled circles are from Hanson and Ravishankara (1991); triangles are from Tolbert *et al.* (1988); and the plus symbols are unpublished data from the SRI laboratory.

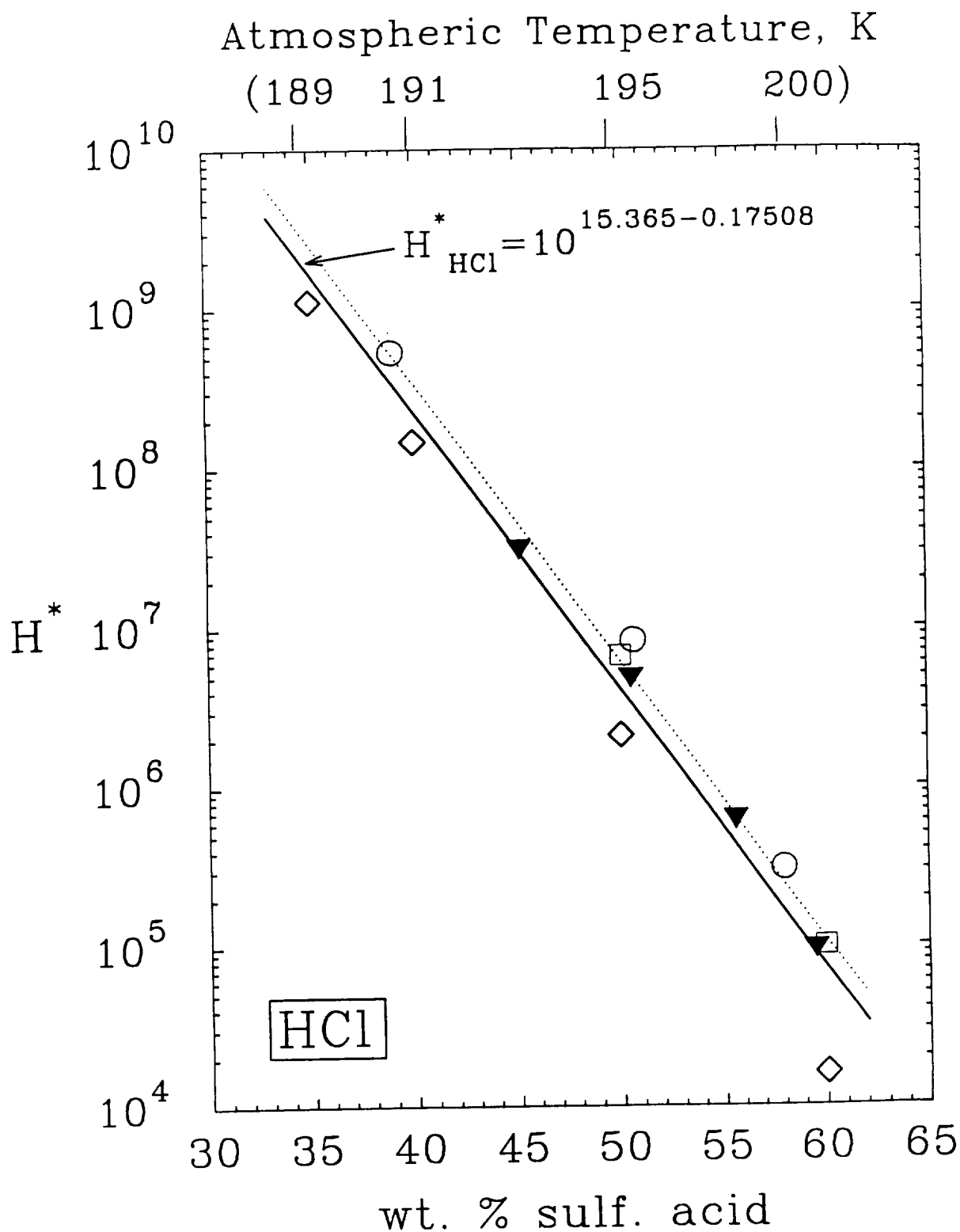


Figure 14. Henry's law constant for HCl in sulfuric acid, as function of wt.% sulfuric acid. Solid triangles from Hanson and Ravishankara (1993a); open circles are calculations of Luo *et al.* (1994); squares from Williams and Golden (1993); diamonds from Zhang *et al.* (1993); and the solid line is a least-squares fit to all the data.

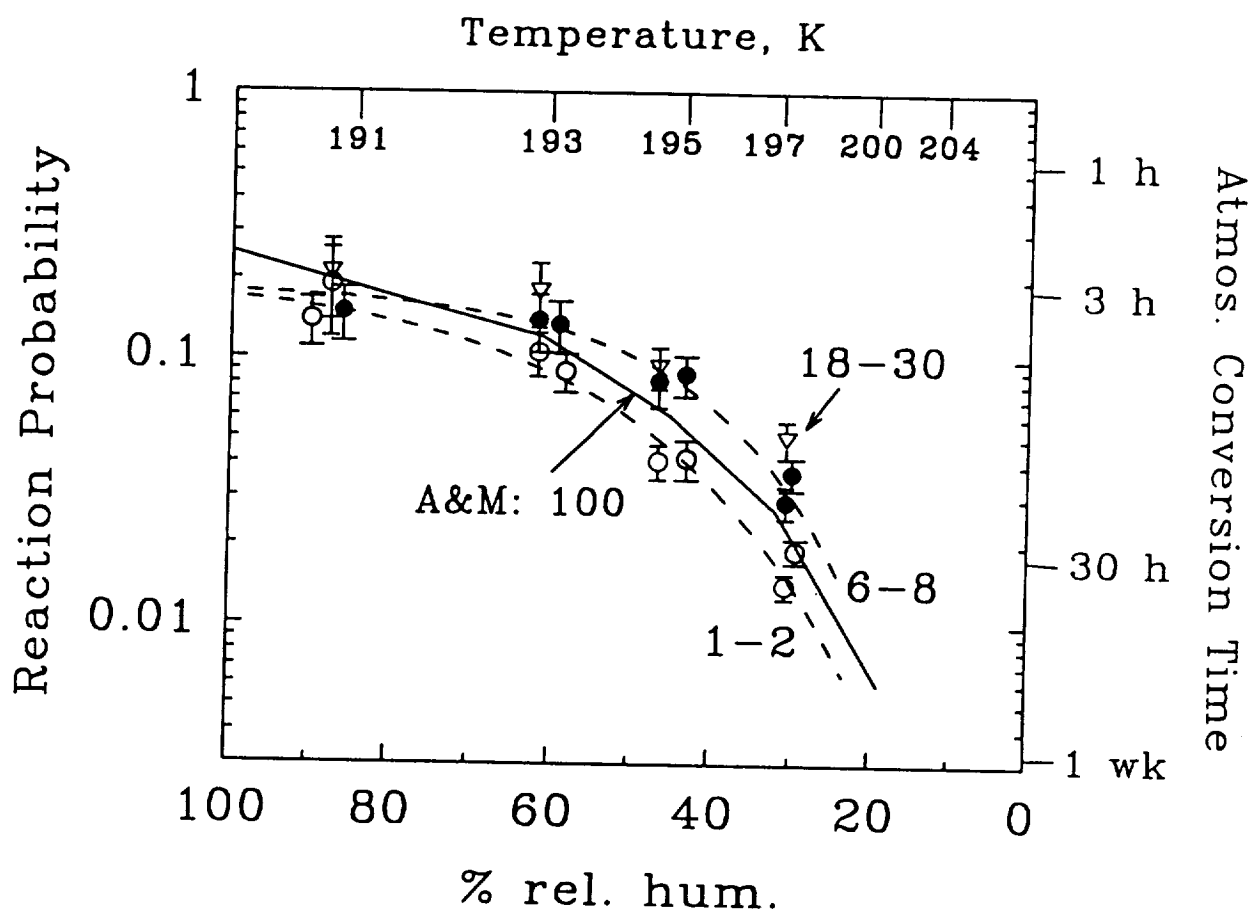


Figure 15a. The reactive uptake coefficient for the reaction of ClONO_2 with HCl on NAT. The level of HCl is noted next to the lines. The data are from Hanson and Ravishankara (1993b) and the line is from Abbatt and Molina (1992).

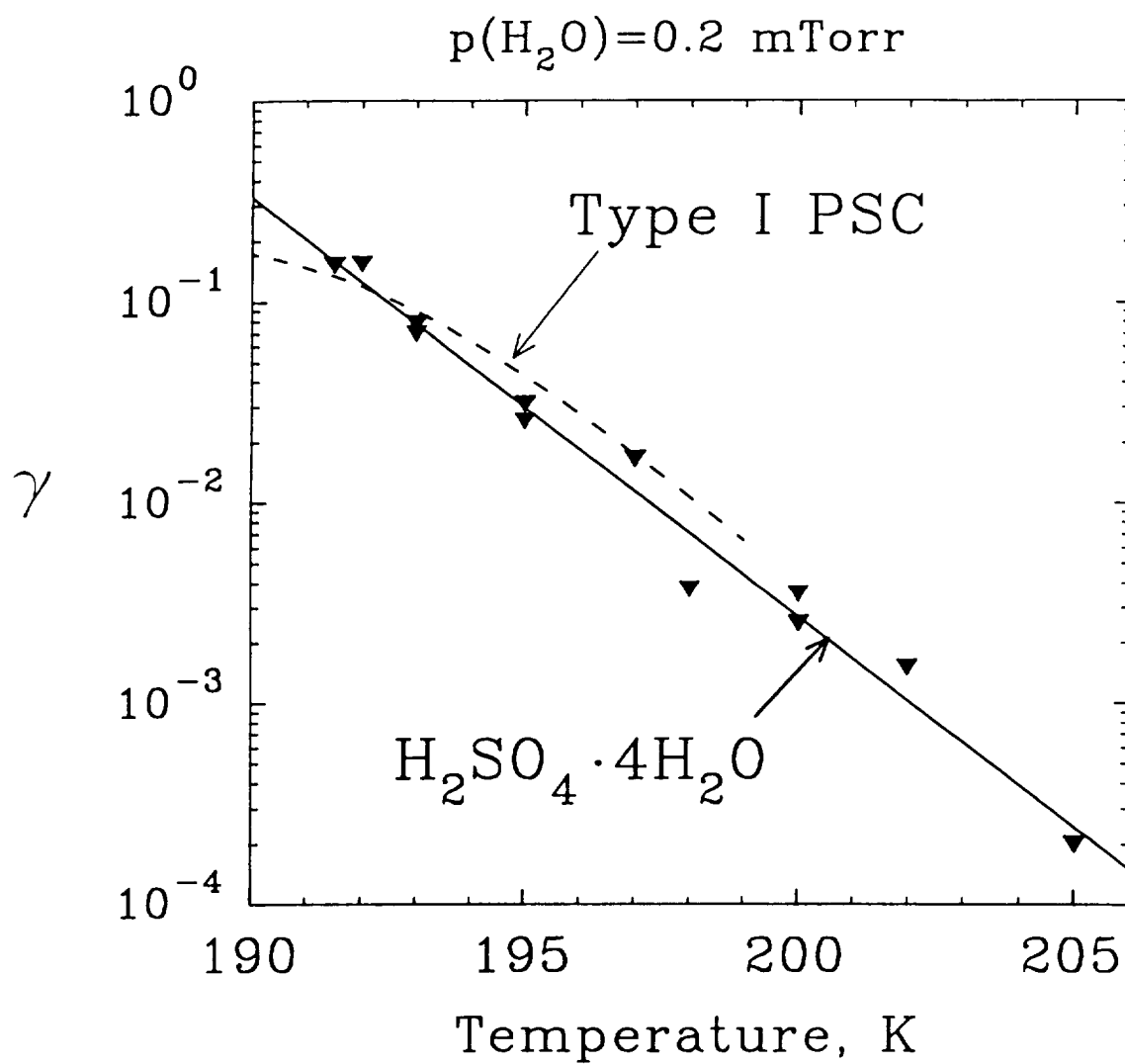


Figure 15b. The reactive uptake coefficient for the reaction of ClONO_2 with HCl on SAT. The data are from Hanson and Ravishankara (1993b) and the line is from Abbatt and Molina (1992).

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MODELING STRATOSPHERIC AEROSOL: PRESENT AND FUTURE

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Rapporteur: David Considine
Principal Speakers: Richard Turco and Malcolm Ko
Other Contributors: Daniel Murphy, David Considine, Randy Kawa, Guy Brasseur, Ross Salawitch, Ivar Isaksen

Modeling stratospheric ozone changes due to anthropogenic emissions is the centerpiece of any assessment activity. Such modeling has been carried out for decades and, gradually, has improved a great deal. The treatment of transport and chemistry in current models is quite sophisticated. It is currently believed that transport is one of the weak links in ozone assessment modeling and, hence, efforts to incorporate three-dimensional models have been initiated. In both two-dimensional and three-dimensional models, treatment of gas phase chemistry and photochemistry is well developed. However, the treatment of heterogeneous chemistry is highly parameterized and the validity of such an approach is not well-known. Another weak link, probably as bad as the transport problem, is the treatment of heterogeneous reactions in these models. This session centered on how the required heterogeneous chemistry can be better represented in models. Further discussions of assessment modeling activities were carried out in a 1-day workshop organized by J. Rodriguez (see Chapter 4 for further details).

Microphysics and Microphysical Modeling

Microphysical models consider all the details of the formation of atmospheric aerosols, including nucleation, growth by condensation and coagulation, evaporation, and sedimentation. These models predict the size distribution, surface area, mass, composition, surface reactivity, and uptake of gas-phase species by the modeled aerosols.

In principle, a detailed microphysical modeling package can be plugged into existing multidimensional, photochemical models of the stratosphere. Microphysics codes are as complex as the photochemical models, however, and the resulting combination is currently too computer intensive for assessment purposes.

Important conclusions from the discussions and presentations on microphysical models are listed below:

1. The processes governing the formation of Type I and Type II PSCs and their dependence on SSAs are still unclear. There are significant differences in the calculated composition of aerosols, assuming a binary $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ or a ternary $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HNO}_3$ composition at cold temperatures. In the latter case, as the temperature decreases the HNO_3 concentration increases dramatically; freezing may be initiated by the rapid change in particle composition with temperature or attainment of NAT composition in the particles. As discussed in the previous section, it is not clear as to when the particles freeze and what triggers freezing. Trajectory model calculations and subsequent comparison with ER-2 data indicate that the assumption that Type I PSCs will nucleate whenever the temperature falls below NAT saturation temperature is incorrect. The back-trajectory temperature structure seems to indicate that the phase of SSAs determines the likelihood of PSC nucleation (i.e., PSC formation is enhanced if SSAs are frozen). Therefore, PSC formation in a parcel will be dependent on the past temperature history of the parcel. Model/ER-2 data intercomparisons indicate that SSAs freeze at or below temperatures where the atmosphere is saturated, with respect to NAT, and that SSAs melt at significantly higher temperatures. These data are consistent with some laboratory data, as discussed in the previous section.

2. The nucleation rate of SSAs is very hard to predict, but it is probably relatively unimportant. The final particle size distribution is likely driven by other microphysical processes.
3. Size distribution of SSAs and PSCs is not log-normal. Using fits to log-normal distributions to determine surface areas from measured mass loading can be erroneous by as much as a factor of two.
4. Surface reactivity of PSCs is a strong function of the local relative humidity and the growth/evaporation phase of PSCs.

There are a few implications of the above findings to aircraft assessment modeling activities. First, predictions of heterogeneous chemical effects are dependent on zonal variability and the past temperature history of the air parcels. The two-dimensional assessment models do not presently account for zonal variability. Trajectory models and three-dimensional models with a microphysical package will be the most capable of determining the implications of heterogeneous chemistry. In the interim, it is important to use microphysics/trajectory models to produce parameterizations of PSC behavior from a statistical analysis of the average zonal effects for use in the assessment models.

Second, use of a coupled, three-dimensional/microphysics code in an assessment mode is at least five years away due to computational difficulty. For now, the results from these models can only be used to occasionally compare with those of assessment models to identify areas of concern and obtain some qualitative answers.

Representation of Heterogeneous Processes in Assessment Models

The models currently being used to assess the impact of perturbations to the stratospheric system are two-dimensional, zonal-mean, photochemical models (e.g., Ko and Douglass, 1993; Prather *et al.*, 1991). The current representation of heterogeneous processes in assessment models does not include detailed microphysics. The parameterization used has the following characteristics:

1. Zonal asymmetries are not addressed. Concentrations of the various trace species are determined using zonal-mean temperature, pressure, and ozone. Rates of gas-phase bimolecular reactions are determined from the product of their zonal-mean concentrations.
2. Heterogeneous reactions are incorporated as first-order loss rates dependent on an aerosol "sticking coefficient," local zonal-mean aerosol surface area, temperature, and concentrations. This parameterization masks all of the microphysical details. Trace-gas concentrations in the aerosols are assumed to be small, except for denitrification by PSCs. Surface area densities for SSAs and PSCs may be either fixed or computed using parameterization. The hydrolysis of N_2O_5 on SSAs is the best understood heterogeneous reaction for assessment modeling. Because of the relative temperature independence of this reaction, there is a fair amount of confidence that the assessment models capture the effects of this reaction correctly. Hydrolysis of ClONO_2 in sulfate is thought to be unimportant at background sulfate concentrations, but will become increasingly more important as sulfate loading increases and for temperature decreases, especially at high latitudes. The proper treatment of PSCs and the influence of vortices air on mid-latitudes is unclear at the present time.
3. No special coupling of the vortices to mid-latitudes, other than that implied by the model circulation and averaged mixing, is attempted.

The concern facing assessment modeling is whether or not the above treatment is adequate to confidently predict the response of the atmosphere to various perturbations. In order to maintain the ability to do decadal time scale runs, an assessment model needs to be fast and relatively simple. The interest in global, rather than local, effects may justify some lack of detail in model formulation.

This need for a fast, relatively simple, assessment model requires that each process be individually evaluated to see if it matters, before the effort is expended, to include it in the assessment models. Such evaluations can be carried out using "process models."

The results of some of the process models show the importance of including more comprehensive heterogeneous chemistry in an interactive way. These results are described below:

1. SSA surface area density increases when the stratospheric aircraft fleet is flown, with estimates ranging from 48 to 90 percent. Changes in ozone depletion, resulting from the increases, are believed to be small. This suggests that aircraft-induced increases in SSA processing may be neglected in the assessment models, but this conclusion should be tested with models that include a more detailed treatment of chlorine activation (i.e., reactions such as $\text{HCl} + \text{ClONO}_2$, enhancements due to zonal asymmetries in temperature, temperature fluctuations, etc.).
2. Inclusion of PSCs into models apparently reduces the sensitivity of the model ozone response to aircraft perturbations in some models. This coupling may be important, especially when current PSC reactions are included.

There is a need to carefully assess the appropriateness of several assumptions which are currently made in assessment models. These include neglect of zonal asymmetries of temperature and constituent concentrations; use of a bulk "sticking coefficient" approach to determine heterogeneous reaction rates, rather than including microphysical details; coupling of vortex ozone to global ozone; and neglect of radiative effects of aircraft-induced increases in SSA and PSC concentrations.

Process Studies of Heterogeneous Chemistry: Current State of Models and Their Results

Effects of Averaging Temperature Fluctuations: Zonal-mean models typically utilize a zonally-averaged temperature distribution to calculate the weight percent and the heterogeneous processing rates of reactions on SSAs (Considine *et al.*, 1994). This can lead to a significant underestimate of the true zonal mean reaction rate (Murphy and Ravishankara, 1994). The same holds true in trajectory models — the mean reaction rate, calculated using mean trajectory temperature, is much smaller than the mean reaction rate calculated by averaging the instantaneous reaction rates along the trajectory (Murphy and Ravishankara, 1994). In some cases, the errors can be nearly an order of magnitude, but often reach factors of two to five. This illustrates the need to carefully determine the effects of zonal averaging of temperatures in model predictions of ozone depletion due to stratospheric aircraft.

Coupled/Fixed Circulation Model Temperature Differences: Coupled zonal-mean models produce a temperature distribution that can be significantly different from the observed zonal mean temperatures, which are typically used in fixed-circulation models. The temperature differences can result in very different predictions of atmospheric response to perturbations, in particular to SO_2 perturbations from a volcanic eruption. This difference may account for some of the discrepancies between the different assessment model predictions of atmospheric response to aircraft or halocarbon perturbations.

Sulfate Aerosol Heterogeneous Reactions: As SSAs get cooler, they take up water and become more dilute. The surface reactivity of the more dilute aerosols is increased for $\text{ClONO}_2 + \text{H}_2\text{O}$, $\text{ClONO}_2 + \text{HCl}$, and $\text{HOCl} + \text{HCl}$ reactions. These reactions must be included to correctly determine the total heterogeneous processing rates on SSAs.

The ability of an SSA to activate chlorine depends on both the temperature and the solar zenith angle. If the photolysis rate of HNO_3 is large, there is enough NO_2 to rapidly convert active chlorine to ClONO_2 , resulting in little net chlorine activation.

HNO_3 distributions, obtained from Limb Infrared Monitor of the Stratosphere (LIMS) measurements, exhibit large mixing ratios at high latitudes and altitudes in winter. These large mixing ratios are not captured by models with an SSA distribution that cuts off at 30 km. If SSAs are extended to higher altitudes, zonal-mean model HNO_3 profiles are in better agreement with the LIMS data. This suggests that although the surface area density of SSA at these altitudes is small, there is enough there to result in a significant re-partitioning of NO_x in favor of HNO_3 . Further, the strontium-90 data may also be consistent with the presence of a significant amount of aerosols above 30 km (Prather and Remsberg, 1993).

Implementation of Heterogeneous Reactions in the Goddard Three-Dimensional Chemistry Transport Model (CTM): The Goddard three-dimensional CTM is driven by winds from the data assimilation STRATAN. The model attempts to realistically simulate the atmosphere down to synoptic scales. A fairly complete gas-phase chemistry package is included, with a rather simple parameterization of heterogeneous reactions. The system takes about 40 minutes of Cray C90 time per day of integration. The time is evenly split between transport and photochemistry, with the photolysis computation dominating the photochemistry part of the computation. Because of the large computer resources required, assessments with this model are not possible at this time.

Accounting for Temperature Asymmetries in a Zonal-Mean Model: Zonal-mean models use zonal-mean temperatures in their calculations. The prediction of PSC occurrence is complicated by this fact, because PSCs can occur in regions of the atmosphere where the zonal mean temperature exceeds the local PSC formation threshold. It is possible to use climatological information in order to more correctly predict the occurrence of PSCs in a zonal-mean model. Fairly good agreement can be obtained between model PSC occurrence and SAM II measurements, using frequency distributions of temperature occurrence, as a function of latitude, altitude, and month, as obtained from National Meteorological Center (NMC) temperature data. This suggests that a simple and fairly reasonable method exists to account for zonal asymmetries in a zonal-mean assessment model.

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HETEROGENEOUS CHEMISTRY IN THE TROPOSPHERE

Session Chair: Paul Crutzen
Rapporteurs: Jack Calvert and Jos Lelieveld
Principal Speaker: Daniel Jacob
Other Contributors: Jos Lelieveld, John Ogren, and Anne Thompson

From synoptic observations, it is known that about 55 percent of the Earth is overcast at any instant. Clouds contain a six to seven percent volume fraction of the troposphere, of which cirrus accounts for about two percent (Table 3). Most cloudiness occurs in the lower troposphere (e.g., stratocumulus), so that clouds contain roughly 10 percent of the mass of the troposphere. If we assume an average cloud thickness of 500 m, a droplet number concentration of 100 cm^{-3} , and a droplet radius of $10 \text{ }\mu\text{m}$, we obtain an air column droplet surface of $30 \text{ cm}^2/\text{cm}^2$, equivalent to a liquid water path of about 100 g m^{-2} , which is roughly in the range derived from satellite observations. Hence, the mean droplet surface in the troposphere is 30 times the underlying Earth's surface, suggesting that there is a considerable area present on which heterogeneous processes can take place. Moreover, as a consequence of the turbulent nature of the troposphere, there is a rapid exchange between the clouds and their surroundings, so that air parcels are frequently exposed to an aqueous environment.

Table 3. Zonally-averaged cloud coverage, estimated using NCAR cloud atlases.

Latitude	90-60°S	60-30°S	30-0°S	0-30°N	30-60°N	60-90°N
Cb %	0.1	0.2	0.3	0.3	0.2	0.1
Cu %	1	4	7	7	3	1
As/Ac %	26	25	23	23	22	23
Ns %	14	9	3	3	7	13
Sc/St %	35	35	22	19	27	31
Ci %	22	26	15	18	20	23
Vol. %*	8-9	~ 7	~ 5	~ 5	~ 6	7-8

* Estimated volume fraction of all cloud types covering a column of tropospheric air
Cb = cumulonimbus, Cu = cumulus, As = altostratus, Ac = altocumulus,
Ns = nimbostratus, Sc = stratocumulus, St = stratus, Ci = cirrus

A similar argument applies to aerosol particles. From aerosol optical thickness observations by satellites, for example, we know that large areas in the remote marine troposphere are affected by soil-derived mineral dust. Unfortunately, such observations are lacking over the continents. Apart from measurements in urban environments, there is no systematically collected information available about tropospheric aerosols, particularly in the free troposphere. In general, it can be stated that if we are to predict tropospheric chemistry and climate perturbations by subsonic aircraft, we require systematic observations to establish climatologies of aerosol abundances, particularly in the parts of the troposphere that are not directly affected by anthropogenic activities.

Our knowledge of the heterogeneous chemistry of the stratosphere has been built upon the observations made in many well-planned field and laboratory studies, focused on ozone destruction mechanisms in the polar and sub-polar regions. Satellite instruments have been developed to study and monitor the chemistry of the upper atmosphere. Equivalent research

efforts are needed in the troposphere. In view of the very much larger surface areas of the ubiquitous tropospheric aerosols, compared to those in the stratosphere and the complex and diverse chemical compositions of these particles, it would be remarkable if their role in tropospheric chemistry would prove to be unimportant. There is a wealth of information related to the homogeneous gas-phase mechanisms of ozone generation and destruction within the polluted lower troposphere. However, knowledge about the degree to which heterogeneous processes contribute to tropospheric chemistry is unsatisfactory.

Predictions of the consequences of subsonic aircraft exhausts on the atmospheric environment may eventually depend upon our ability to simulate these with three-dimensional, global, coupled-chemistry/climate models. In the interim, as in the case of the stratosphere, two-dimensional models, with insights from process models, may have to be used. A particularly important requirement is that these models resolve, with sufficient accuracy, the middle troposphere from the upper troposphere and lower stratosphere, where the effects are expected to be largest. For example, an increase in upper tropospheric O_3 in the tropics is expected to exert a relatively strong climate forcing effect. However, the models cannot yet resolve the contributions to the O_3 in the troposphere due to the downward transport from the stratosphere and due to local production. The estimate for stratospheric contributions, on a global scale, ranges between 200 and 900 Tg yr⁻¹ which, depending on the model, could be a factor of two smaller or larger than the estimated net photochemical production in the troposphere.

Our understanding of the middle and upper tropospheric NO_x budget is limited, even though this issue is vital to the quantification of O_3 perturbations by subsonic aircraft. Measurements seem to systematically indicate that the NO_x abundance is higher than what we would expect based on current modeling efforts. This may indicate a "missing source." Lightning NO_x production would be a possibility, although the rather uniform NO_x distribution often measured seems to preclude an inhomogeneous source. Release of NO_x from "reservoir" species, such as volatile organic nitrates and/or aerosol-born compounds should also be considered. Furthermore, the vertical transport of NO_x and other trace species through deep convection should be quantified.

Several case studies have shown that venting of polluted air from the boundary layer into the upper troposphere enhances the O_3 formation efficiency of surface emitted NO_x . Pollutant plumes from fossil fuel or biomass combustion can be carried rapidly from the lower into the upper troposphere, which increases the long-range transport of O_3 precursors and particulate material.

Measurements in the marine boundary layer, although relatively scarce, suggest that models generally underestimate H_2O_2 concentrations. The photochemical formation of this gas is particularly sensitive to the mixing ratios of NO_x and other O_3 precursors, such as reactive hydrocarbons, so that the model disagreement with measurements is indicative of problems with calculations. Several recent studies suggest that transition metals (e.g., Fe^{2+} , Cu^{2+}) in aerosols and clouds can scavenge HO_x molecules, yielding H_2O_2 in catalytic chemical cycles. On the other hand, photocatalysis of iron-hydroxy complexes may produce HO_x radicals in the droplets. The net result of these reaction sequences is still unclear. Laboratory work on the redox reaction mechanisms involving transition metals, ligand complexes, and *in situ* tropospheric measurements are needed to evaluate the importance of these mechanisms.

Clouds can significantly alter the chemical processes in the air parcels in which they occur. Acid formation, in particular that of sulfuric acid from SO_2 , is strongly enhanced in the cloud liquid-phase, which reduces the pH. Because some radicals are soluble in cloud water, liquid-phase reaction sequences can become important and the outcome can be appreciably different from those under cloud-free circumstances. Some gases are so soluble that they largely go into the droplets, while others stay within the interstitial gas phase. For example, HO_2 largely

dissolves, while NO is rather insoluble; therefore, the reaction between the two species in the gas phase, which is a major ozone source, can become negligible in the presence of the droplets. Furthermore, formaldehyde is rapidly destroyed by aqueous-phase oxidation such that the gas phase concentration of this important precursor of HO_x radicals can be depleted. Thus, it appears that cloud chemistry could reduce O₃ formation in the troposphere. On the basis of modeling studies which include such processes, it has been predicted that O₃ destruction reactions in clouds may be enhanced. However, recent laboratory work has raised questions about this conclusion. It is not even clear if the volume of clouds in the troposphere is large enough to significantly alter the global scale O₃ concentration. Laboratory, field, and modeling research is required to clarify these discrepancies and also to evaluate the importance of cirrus clouds in the photochemistry of the troposphere.

Several studies have shown that N₂O₅ scavenging by clouds and aerosols is a significant sink for NO_x. The reaction on aerosols appears to be most important in the industrially-affected, aerosol-rich part of the Northern Hemisphere, while in relatively unperturbed regions clouds are more important. However, in some areas, wind blown mineral dust may act as a nighttime NO_x sink. There is some indirect observational evidence which supports such a conclusion. It has been shown that the mid-latitude, wintertime transport of nitrogen oxides from polluted regions and their deposition are almost equal to those in the summer, even though there is no significant seasonality in industrial NO_x emissions and the photochemistry is different. This inconsistency is explained by the more effective N₂O₅ removal during relatively cold and long winter nights, which substitute for the summer process of daytime NO₂ oxidation by OH. Both these reaction mechanisms limit the NO_x lifetime to a few days. Since significant heterogeneous NO_x destruction is expected to have a negative effect on photochemical O₃ formation, these processes need to be quantified in more detail.

Aerosol particles, which include (NH₄)₂SO₄, and NH₄HSO₄, are usually assumed to have taken up water and, thus, be spherical. However, water vapor observations in the free troposphere suggest that, particularly in the subtropics, relative humidities can be low enough for the aerosol particles to remain as solids. Measured reaction probabilities, for example those of N₂O₅ on aqueous aerosols, may not be applicable to these particles, which suggests a need for laboratory studies which simulate these conditions of water vapor and temperature. Also, the light scattering properties of dry aerosol are bound to be different from those of deliquesced spherical droplets. In fact, even the optical effects of deliquesced particles are rather uncertain, although such information is imperative for estimates of aerosol climate forcings. Therefore, simultaneous measurements of aerosol size distributions, chemical compositions, and optical properties are sorely needed.

Recent measurements in the Arctic troposphere indicate a relation between very low O₃ concentrations (lower pptv range) and the presence of halogen species; in particular, species containing Cl and Br. The sources of the halogens are quite uncertain; excretion by marine phytoplankton is considered to be a potential source of organic halogens. Once in the atmosphere, photochemical and/or heterogeneous processes may release reactive Cl and Br which, in turn, could destroy O₃. It should be investigated whether heterogeneous mechanisms under very cold tropospheric condition could be important. It is recommended that the Arctic region be considered as a "natural laboratory" and further studies be carried out.

On the basis of measurements in the marine boundary layer, it has been suggested that heterogeneous chemistry in deliquesced sea salt particles activates reactive chlorine by reaction of O₃(a) with Cl⁻. Photolysis of the released reaction product (Cl₂) yields Cl radicals in the gas phase. Cl atoms react very rapidly with many gases and, potentially, contribute significantly to marine, boundary-layer photochemistry. From stratospheric chemistry studies many of the

reaction products of Cl/Br chemistry are known, so that observational studies could provide critical tests of the importance of these mechanisms. In particular, field measurements of HOCl and HOBr are expected to be of great value in this respect.

SUMMARY OF WORKSHOP FINDINGS

This section provides a concise summary of workshop findings. In addition, many problems that were not directly addressed in the workshop, but that directly relate to the atmospheric effects of aircraft, are included to present a more complete picture. Lastly, general recommendations, which are not specifically addressed in the next section, are included.

One cannot predict the eruptions of volcanoes, which are the major source of SO_2 into the stratosphere. Therefore, one has to assess the effects of any perturbation under a variety of stratospheric sulfate loading. There is some uncertainty regarding the level of sulfate aerosol loading that could be reached in the case of prolonged absence of volcanic injections. In addition to volcanoes, the transport of tropospheric sulfur is known to be a source of stratospheric sulfur. As argued earlier, frequent volcanic injections have made this source negligible in the past two decades. The level of sulfate loading expected to be present when only COS contributes is uncertain. This level may be called the "background" level. Clear, quantitative identification of this level is of great importance for two reasons: this level defines the mark against which emissions of aircraft are to be judged; and more importantly, it defines the level at which the rates of heterogeneous processes and consequences of aircraft emissions are to be evaluated. Derivation of the background levels, solely from extrapolations of observed temporal variation of mass loadings, may not be accurate and needs checking. In the absence of a clear-cut answer to this question, assessment models should also be run with mass loadings of one-third of the currently assumed "background" levels.

It appears that our state of understanding of the formation, composition, growth, dissipation, and removal of particles in stratosphere is not adequate to calculate the surface areas and the nature of particles in/on which heterogeneous chemistry takes place. Efforts must be made to improve this situation via laboratory measurements, field observations, and modeling. Also, enhancement of the microphysical models to realistically simulate the atmosphere requires some major break-through in understanding nucleation phenomenon. Currently, it is believed that the source of new particles is the homogeneous nucleation of gas-phase sulfuric acid. Yet, it is not completely clear to what extent gas phase sulfuric acid is indeed formed in the oxidation of SO_2 in the presence of particles. Any special nucleating properties of aircraft emitted particles could play a major role. Very little is known about this possibility.

In the absence of the capability to predict the surface area of sulfate aerosols available for heterogeneous chemical reactions in the stratosphere, we have to rely on past observations to determine the extent of heterogeneous processing that can take place. Since aerosol loading can vary from so-called "background" to high values (due to volcanic eruptions), one has to estimate the effects at the limits of the loading, as well as a few intermediate values. As noted above, calculations at sub "background" levels are also very useful. It is also important to determine if aircraft emissions themselves could substantially enhance sulfate loading.

The situation regarding PSCs is somewhat different. There is some uncertainty as to the degree of supersaturation required for the formation of Type I PSCs, and the formation conditions seem to vary between poles. The thermodynamic limit appears to be a reasonable indicator, not a definitive milestone. One of the major findings of the workshop was that the so-called Type I PSC may not always be solid $\text{H}_2\text{O}/\text{HNO}_3$ ice. In some cases, they may be liquid ternary solutions containing H_2SO_4 , HNO_3 , and H_2O . It appears that it would be feasible to predict the formation of PSCs in the near future, if the sulfur level and conditions required for nucleation are understood. Laboratory studies, aimed at determining the exact requirements for the formation of PSCs, would further this cause to a great extent. Satellite observations, near the

vortex edge, and coverage over a longer time frame are greatly needed. *In-situ* observations of PSCs, with emphasis on composition, shape, size, and condensation nucleus would be very useful.

As in the case of sulfate aerosols, for the near future, it is necessary to use climatology from satellite and *in-situ* data. Use of thermodynamics to determine the extent of PSC formation may be appropriate.

Laboratory studies have increased our understanding of a great deal of heterogeneous chemistry in the stratosphere. These studies, coupled with field observations, are a powerful way to investigate and, hopefully, answer when, where, and in what form stratospheric particles are formed. Currently, there is a nebulous temperature range where we cannot be sure as to what the particles are (i.e., are they liquid sulfuric acid aerosols, frozen sulfuric acid aerosols, ternary mixtures of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HNO}_3$, or some other phase of $\text{HNO}_3/\text{H}_2\text{O}$). In addition, it is not clear if freezing of sulfate aerosols is necessary for the nucleation of PSCs. Also, it is not completely clear when sulfate aerosols freeze and, once frozen, when they turn back into liquids. This region of uncertainty is between ~ 189 K and ~ 220 K. Unfortunately, this is also the regime where the role of heterogeneous processing will be greatly enhanced. It appears that the rates of the conversion of ClONO_2 and HCl to active chlorine, via heterogeneous chemistry, does not have an extreme jump at a special temperature. This is because, the sulfate aerosols process chlorine compounds with a high degree of efficiency, approaching that of PSCs, as the temperatures approach PSC formation threshold. However, since the surface areas of the PSCs are greater than those of SSAs (even after they have swelled due to water uptake), PSC processing rates would be faster in the atmosphere. The formation of Type II PSCs appear to be crucial for the denitrification process. Even though the sulfate aerosols appear to take up HNO_3 , the formation of the ternary mixtures will not lead to the removal of HNO_3 and, hence, NO_y and NO_x from that region of the stratosphere. Thus, even if the chlorine activation rate is not too different between PSCs and sulfate aerosols, denitrification, caused by the formation of Type II PSCs, will control the gas-phase abundance of reactive chlorine and nitrogen compounds in the atmosphere. Another aspect that should be borne in mind is the role of PSCs when atmospheric chlorine levels are low (i.e., natural levels in the next century); this should also be addressed.

By necessity, assessment modeling and, to a large extent, stratospheric modeling have, until now, treated heterogeneous chemistry as an "add-on" to the gas-phase-only model, by representing such reactions by a first-order reaction rate coefficient. This approach must change and, indeed, it is changing to include heterogeneous reactions in a completely interactive fashion with gas-phase chemistry. This is a major first step, and future progress along these lines is anticipated.

There are many other major assumptions and omissions that greatly alter the calculated contribution of heterogeneous reactions. These include assuming zonally-symmetric temperatures and species concentrations. Assumption of a constant temperature, in a parcel of air as it moves, will underestimate the extent of heterogeneous conversion of chlorine from non-reactive to active forms. The transport of air from, and to, the polar vortices can be major cause of altered partitioning in chlorine and nitrogen species. Since it is unlikely that all asymmetries can be realistically included in assessment models in the near future, process models need to assess and quantify the errors introduced by the assumptions and omissions. The 1-day modeling workshop addressed all of these issues.

Our understanding of heterogeneous chemistry in the troposphere is very fragmentary and rudimentary. In the case of the stratosphere, the discovery of the ozone hole and the subsequent intensive research carried out to unravel this phenomenon led to great advances in this field. A similar concerted effort may be needed to better understand and quantify the role of heterogeneous chemistry in the upper troposphere. A few examinations have already shown that

the effect of heterogeneous chemistry on upper-tropospheric ozone levels can be dramatic. In the absence of a great deal of information, it appears prudent to first take stock of what is clearly known and what is needed in the near future. One major thrust has to be to characterize the aerosols that are already in the upper troposphere and their reactivity in this region. Cloud processing has to be another major area of investigation.

IDENTIFIED AREAS OF UNCERTAINTY AND RECOMMENDED FUTURE WORK

Climatology of Aerosols and PSCs

1. Obtain more observations to improve the climatology of PSCs, especially in the polar night regions where observations have been limited to date
2. Determine the physical nature (i.e., ice, NAT, etc.) of the observed PSCs
3. Improve our understanding of when, where, and how PSCs form and dissipate
4. Better quantify PSC surface area at the edge of, and just outside, polar vortices
5. Verify if the size variation of stratospheric aerosols, with decreasing temperature, is consistent with expected swelling due to the uptake of water by (and dilution of) sulfuric acid solution droplets
6. Identify the reasons for discrepancies between satellite-derived and *in-situ* measurements of aerosol properties in the lowest part of the stratosphere (15 km and below)
7. Identify the physical state of sulfuric acid-water aerosols, and determine if there is hysteresis in their freezing and melting
8. Improve our knowledge of the physical chemistry and microphysics of stratospheric aerosols at temperatures < 200 K, including an understanding of the formation of ternary sulfuric acid/nitric acid/water solutions
9. Ascertain how well particle surface areas, determined from *in-situ* or remote optical measurements, reflect the area of chemically active surfaces
10. Determine if there is a trend in the background (non-volcanic) stratospheric aerosol loading with time. If there is, determine the cause(s) of the trend
11. Improve our understanding of the microphysics of particle formation and removal, in general

Laboratory Studies

Microphysics:

1. Properties of ternary mixtures ($\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$), at temperatures below 194 K (to as low as 188 K), should be investigated. The formation of NAT, or metastable higher hydrates, and the freezing characteristics of sulfuric acid should be re-measured.
2. Atmospheric cooling and warming processes should be carefully evaluated. Under closely monitored thermodynamic conditions, evaporation and melting of NAT and SAT should be determined.

3. The formation of NAT and/or metastable hydrates on frozen SAT substrates should be investigated.
4. Even though field measurements were not directly discussed, one of the needs was apparent. Because of the recycling processes of aerosols and PSC particles, balloon and aircraft-borne measurements will greatly benefit from back-trajectory calculations. During the time of measurements, precise temperature data are needed in addition to partial pressures of water vapor and HNO_3 . Further attempts to measure and characterize PSCs (e.g., using IR or UV absorption) may be useful.

Modeling Sulfate Chemistry in the Stratosphere:

1. Henry's law solubility for HCl
2. Directly measured diffusion coefficients in H_2SO_4 , as a function of T and wt.% H_2SO_4
3. Additional measurements of H and k for species in sulfuric acid solutions
4. Reactivity of frozen H_2SO_4 , as a function of composition and relative humidity
5. Other reactions, especially HO_x reactions on sulfuric acid
6. Studies of chemistry and microphysics on actual sulfuric acid aerosols
7. Optical constants of low temperature liquid and frozen sulfuric acid for comparison with field observations
8. Ascertain if the surface is different, in composition and structure, from the bulk of the droplets

Modeling PSC Chemistry in the Stratosphere:

1. Temperature dependence of $\text{N}_2\text{O}_5 + \text{HCl}$ reaction on NAT
2. Measurements of $\text{ClONO}_2 + \text{HCl}$ reaction in the low HCl limit
3. Studies of the morphology of laboratory and actual PSCs to determine the role of internal surface area
4. Reactions on actual PSC particles
5. Measurements of the nucleation of PSCs; determination of phase and composition of PSCs
6. Ascertain if the surface is different, in composition and structure, from the bulk of the particles

Modeling Studies

Substantial questions remain concerning the mechanisms governing the formation of stratospheric aerosols. In addition, the models currently used for assessments do not easily deal with zonal asymmetries and may not represent stratospheric dynamics particularly well. These facts suggest an approach to assessments that will maximize prediction confidence:

1. Models should be constructed to include all known processes concerning the formation and growth of stratospheric aerosols, even though our understanding is incomplete. Processes which are known to be important should be included in a test fashion, even if they are not fully understood. The models should then be constrained as well as possible, using available atmospheric measurements.
2. The model parameter space should be explored as completely as possible. The sensitivity of model predictions to processes, which are not particularly well understood, should be examined closely.
3. The effects of transformations which might possibly make a difference but are not known to be important should also be examined using process models. An example of such a situation is the possibility that models substantially overestimate HCl concentrations. A future atmosphere with a different background chlorine partitioning may respond to an aircraft perturbation in a substantially different manner than current models do; this should be considered.

Tropospheric Chemistry

A. Processes: important, need quantification:

- Convective exchange of short-lived trace species
- Stratosphere-troposphere exchange processes
- Heterogeneous nighttime chemistry of NO_x
- NO_x sources in the middle and upper troposphere

B. Processes: potentially important, not well understood:

- Halogen and heterogeneous chemistry in the marine boundary layer
- Heterogeneous chemistry in cirrus clouds
- Formation and microphysics of aerosols in the upper troposphere
- Role of cloud chemistry in the tropospheric O_3 budget

C. Observations:

- Free troposphere concentrations of trace species, in particular NO_y , O_3 , H_2O , CO , NMHCs, SO_y , and NH_3
- Three-dimensional aerosol climatologies, including information about chemical composition and optical properties, hygroscopicity, size distributions, internal/external mixtures, and CCN subsets

D. Laboratory Studies:

- Reaction mechanisms on ice and aerosol particles
- Heterogeneous chemistry, involving transition metals

- Hygroscopicity of aerosols, as function of chemical composition

E. Model Development:

- Cloud-scale models to study boundary layer, dynamical and microphysical processes and heterogeneous chemistry
- Coupled climate/chemistry models with realistic representations of vertical exchange and heterogeneous processes

APPENDIX A

LIST OF ACRONYMS

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LIST OF ACRONYMS

AAOE	Airborne Antarctic Ozone Experiment
AASE	Airborne Arctic Stratospheric Expedition
CCN	Cloud Condensation Nucleus
CN	Condensation Nucleus
COS	Carbonyl Sulfide
CTM	Chemistry Transport Model
DIAL	Differential Lidar
IR	Infrared
LS/UT	Lower Stratosphere/Upper Troposphere
LIMS	Limb Infrared Monitor of the Stratosphere
NAD	Nitric Acid Dihydrate
NAM	Nitric Acid Monohydrate
NAP	Nitric Acid Pentahydrate
NASA	National Aeronautics and Space Administration
NAT	Nitric Acid Trihydrate
NCAR	National Center for Atmospheric Research
NMC	National Meteorological Center
NOAA	National Oceanic and Atmospheric Administration
PNA	Pernitric Acid
PSC	Polar Stratospheric Cloud
QBO	Quasi-Biennial Oscillation
SAGE	Stratospheric Aerosol and Gas Experiment
SAM	Stratospheric Aerosol Measurement
SAT	Sulfuric Acid Tetrahydrate
SSA	Stratospheric Sulfate Aerosols
SST	Supersonic Transport
UV	Ultraviolet
WMO	World Meteorological Organization

APPENDIX B

MEETING AGENDA AND LIST OF ATTENDEES

**Heterogeneous Chemistry Workshop
8-10 November 1993
Boulder CO**

Agenda

Monday, 8 November 1993

8:30-8:45 am	Welcome	Rich Stolarski/ Jack Kaye Ravishankara
8:45-9:15 am	What is to be covered in the workshop and what we need to get out of the workshop	

SESSION I: OBSERVATION OF STRATOSPHERIC PARTICLES
CHAIR: David Fahey; RAPPORTEUR: Chuck Brock

9:15-10:00 am	Satellite Observations of PSCs and Sulfate aerosols	Lamont Poole
10:00-10:30 am	<i>Break</i>	
10:30-11:15 am	Balloon and Aircraft Measurements of PSCs and Sulfate Aerosols	Terry Deshler
11:15 am-12:15 pm	Discussion and Short Presentations	
12:15-1:15 pm	<i>Lunch</i>	

SESSION II: LABORATORY OBSERVATIONS
CHAIR: Konrad Mauersberger; RAPPORTEUR: Maggie Tolbert

1:15-2:00 pm	Laboratory Studies of Nucleation and Reactions on PSCs	Mario Molina
2:00-2:45 pm	Laboratory Studies of Reactions in Sulfuric Acid	David Hanson
2:45-3:15 pm	<i>Break</i>	
3:15-4:15 pm	Discussion and Short Presentations	
4:15-5:00 pm	Discussion of Day's Presentations	

Tuesday, 9 November 1993

SESSION III: MODELING HETEROGENEOUS CHEMISTRY
CHAIR: Susan Solomon; RAPPORTEUR: David Considine

8:30-9:15 am	Microphysical Models	Rich Turco
9:15-10:00 am	Heterogeneous Chemistry in Assessment Models	Malcolm Ko
10:00-10:30 am	<i>Break</i>	
10:30 am - 12:00 n	Discussion and Short Presentations	
12:00 n - 1:00 pm	<i>Lunch</i>	

SESSION IV: TROPOSPHERIC HETEROGENEOUS CHEMISTRY
CHAIR: Paul Crutzen; Rapporteurs: Jack Calvert, Jos Lelieveld

1:00-1:45 pm	Tropospheric Heterogeneous Chemistry	Daniel Jacob
1:45-3:00 pm	Short Presentation	
3:00-3:30 pm	<i>Break</i>	
3:30-4:00 pm	Discussion and Short Presentations	
4:00-5:00 pm	Discussion of Day's Presentations	

Wednesday, 10 November 1993

SESSION V: SUMMARY

CHAIRS: *Ravishankara/Rich Stolarski/Jack Kaye/Anne Thompson*

8:30-8:50 am	Paul Crutzen, Jack Calvert, and Jos Lelieveld
8:50-9:20 am	Discussion
9:20-9:40 am	David Fahey and Chuck Brock
9:40-10:10 am	Discussion
10:10-10:30 am	<i>Break</i>
10:30-10:50 am	Konrad Mauersberger and Maggie Tolbert
10:50-11:20 am	Discussion
11:20-11:40 am	Susan Solomon and David Considine
11:40 am - 12:10 pm	Discussion
12:10-12:30 pm	Overall Summary
12:30 pm	<i>Adjourn</i>

Assessment Model Workshop

11 November 1993

Boulder, CO

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APPENDIX C

SUMMARY OF TALKS

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On the Formation of Polar Stratospheric Clouds

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A summary was presented of *in situ* and lidar observations, pertinent to the formation of PSCs in the Arctic and Antarctic. ER-2 observations suggest in the Arctic that the sulfate aerosol may remain liquid until at least the temperature at which PSCs were observed to form, about 192 K. Both balloon-borne and ER-2 observations show the presence in the Arctic of activation of a very small fraction of sulfate particles near NAT saturation, which has the effect of producing a veil of enhanced surface area upon which heterogeneous reactions can occur prior to the main body of the PSC.

Both ER-2 and balloon measurements in the Arctic show that the main onset of PSCs occurs with apparent saturation ratios of 10 or larger. In the Antarctic all observations are in late winter and show formation of PSCs near NAT saturation. The difference between the two hemispheres is important to understand, but may be the result of the previous history of the sulfate particles. Unlike the Arctic where the sulfate seem to be liquid, in the Antarctic late winter sulfate particles may all have crystallized. Lidar depolarization measurements in the Arctic and Antarctic are consistent with this hypothesis.

Model simulations of Arctic PSC formation which assume that the sulfate are crystallized prior to PSC formation consistently predict the formation of a PSC prior to the time they were observed. This was true of the UCLA model of Drdla *et al.*, in comparison to the ER-2 results of Dye *et al.*, and also was true from the Max Planck Institute model of Peter *et al.*, in comparison to the balloon observations of Deshler and Hoffman. These comparisons suggest that the conceptual model of PSCs forming on previously frozen sulfate particles is incorrect, unless we are making some fundamental mistakes on PSC nucleation.

Results of calculations were presented which used the Zhang *et al.* (1992) laboratory results on the uptake of HNO_3 in the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution droplets and also an extrapolation of the parameterization for those results included in the Zhang paper to examine the increase of particle volume with decrease in temperature. These calculated increases in particle volume were insufficient to explain the increases in volume observed by the FSSP on the ER-2. However, during the workshop Thomas Peter presented results contrary to these which suggested that the observed increase in volume might be explained by the uptake of HNO_3 . Although the issue was not resolved during the workshop, it now appears that some of the ER-2 observations could be explained by the rapid uptake of HNO_3 in the solution droplets to form the observed PSC.

Solubility of HBr in and Viscosity of Sulfuric Acid Solutions at Stratospheric Temperatures

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Heterogeneous reactions on the surfaces of stratospheric sulfate aerosol particles may contribute to global ozone depletion in a manner analogous to the heterogeneous chemical processing on polar stratospheric cloud particles preceding the Antarctic ozone hole. Much attention has been devoted to reactions of chlorine containing reservoir molecules. Because bromine atoms also participate in the catalytic destruction of ozone, we have started investigating the heterogeneous interactions of bromine containing species with sulfuric acid surfaces at stratospheric compositions and temperatures.

Uptake coefficients for HBr on sulfuric acid were measured using a Knudsen cell reactor with mass spectrometric detection of the gas phase HBr. The effective Henry's law solubility (H^*) is determined from the time dependence of the uptake coefficient. Typical values of H^* are 1×10^7 M/atm in 60 wt%, 3.7×10^5 M/atm in 66 wt% and 1.3×10^4 M/atm in 72 wt% sulfuric acid. HBr is about 100 times more soluble than HCl for a given temperature and concentration of sulfuric acid. However, very little HBr will be dissolved in the stratospheric sulfate aerosol because of the low gas-phase concentration of HBr in the stratosphere.

Analysis of time-dependent uptake data requires knowing the diffusion constant in the liquid which is estimated from the viscosity of the sulfuric acid. We have measured the viscosity of 30 to 80 wt% sulfuric acid at temperatures between 200 and 300 K. The viscosity increases sharply at low temperatures and can be modeled with a semi-empirical four-parameter equation.

Research supported by NASA Upper Atmosphere Research Program.

FTIR Studies of Model PSC Nucleation on Sulfuric Acid Films

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Using Fourier transform infrared (FTIR) spectroscopy, we performed laboratory experiments designed to simulate polar stratospheric cloud (PSC) formation on stratospheric sulfate aerosols (SSAs). Our experimental apparatus consists of a vacuum chamber containing a temperature-controlled silicon substrate. Sulfuric acid films were produced on the silicon substrate by the condensed-phase reaction of SO_3 with H_2O (Middlebrook *et al.*, 1993). The H_2SO_4 films were subsequently exposed to H_2O and HNO_3 vapors and cooled to observe changes to the film due to gas uptake and condensational growth. The phase and composition of the H_2SO_4 film and the identity of the condensing species were determined from transmission FTIR spectra (Koehler *et al.*, 1992; Middlebrook *et al.*, 1993). Specifically, we studied nitric-acid/ice growth on sulfuric acid tetrahydrate (SAT) and on supercooled liquid H_2SO_4 films (Iraci *et al.*, 1994).

For the first experiment, a SAT film was formed by cooling a sulfuric acid film in the presence of H_2O vapor until the infrared spectrum indicated that the film was frozen. The SAT film was then exposed to $P_{\text{H}_2\text{O}} = 3 \times 10^{-4}$ Torr and $P_{\text{HNO}_3} = 2.3 \times 10^{-6}$ Torr at 192 K. After 2 hours, the infrared spectrum contained peaks characteristic of both SAT and α -NAT (nitric acid trihydrate). This experiment demonstrated that crystalline NAT films could nucleate on SAT. Other experiments indicated that sulfuric acid hemi-hexahydrate (SAH) could also provide a surface for NAT condensation.

In the second experiment, a supercooled liquid sulfuric acid film was cooled to 191.5 K. The infrared spectrum of the film just after cooling indicated that the film was approximately 54 wt % sulfuric acid. After 1.5 minutes of exposure to $P_{\text{H}_2\text{O}} = 3 \times 10^{-4}$ Torr and $P_{\text{HNO}_3} = 2.3 \times 10^{-6}$ Torr, the infrared spectrum indicated that the film had taken up HNO_3 . After 8 minutes, a sharp infrared peak at 1370 cm^{-1} characteristic of α -NAT appeared in the infrared spectrum. These results demonstrate the uptake of HNO_3 by sulfuric acid at low temperature. Furthermore, we believe that the formation of crystalline NAT in the presence of supercooled sulfuric acid was due to homogeneous nucleation from the ternary $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ liquid without freezing of the entire solution. Therefore, the freezing of SSAs may not be a requirement for PSC formation.

Finally, we examined the effect of warming the mixed NAT/supercooled H_2SO_4 film at 1 K/min in the presence $P_{\text{H}_2\text{O}} = 3 \times 10^{-4}$ Torr and $P_{\text{HNO}_3} = 2.3 \times 10^{-6}$ Torr. By 197 K, the supercooled sulfuric acid film crystallized to SAH. By 201 K, NAT was clearly evaporating and SAH had converted to SAT. NAT had completely desorbed by 205 K and the SAT film remained stable until it melted at 211 K. These results suggest that if SSAs do not freeze before PSCs condense, they may crystallize upon warming as PSCs evaporate.

The above experiments indicate that the most likely composition of type I PSCs is NAT. However, it is possible that NAT was able to condense on H_2SO_4 films because the saturation ratios (S_{NAT} = the partial pressure of HNO_3 divided by the vapor pressure of HNO_3 over NAT) for these experiments were very high ($S_{\text{NAT}} \leq 270 - 590$). Therefore, more experiments are currently being performed using saturation ratios closer to those observed for actual PSC formation ($S_{\text{NAT}} = 1$ in the Antarctic stratosphere, $S_{\text{NAT}} \sim 10$ in the Arctic).

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Heterogeneous Chemistry and Ozone: What is in Assessment Models?

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Mechanisms in 2-D Assessment Models versus 3-D Process Models

Obviously, more details in 3-D models.

- Do details affect the large scale behavior, given that the lifetime of ozone in the lower stratosphere is long?
- Lack of the third dimension: can extra details be incorporated in a meaningful way?
- Constraint on computer resources: process model simulate months; assessment model simulate years.

Approaches in 2-D Stratospheric Assessment Models

- Standard approach for reaction on aerosol:
 - Heterogeneous reactions are parameterized as first-order rates, dependent on local surface area (zonal-mean) (A); reaction probability γ (parameterized by zonal mean, T ; and H_2O)
 - It is assumed that the amount of trace gas trapped in the solid is small, compared to the burden in gas phase
 - Some models attempt to calculate aerosol surface area from gas phase H_2SO_4 burden and micro-physics
- PSC chemistry, (not fully integrated into assessment model yet):
 - Temperature distribution to get NAT formation, keep track of gas sequestered
 - Not at all clear how ozone changes in the vortex affect ozone at mid-latitudes

Questions

- How to deal with zonal asymmetry? Is it important?
- How is vortex connected to mid-latitude?
- Is it important to predict changes in aerosol and PSCs? How does the change affect dynamics and chemistry?

Approach

- Work through process models to get validation of mechanism and sensitivity of results to parameters (how accurate do we need to know them?)
- Need to go to 3-D, at least in a limited way, to see if 2-D approach is viable
- Implement in assessment model accordingly

Chapter 4

Assessment Model Workshop Summary

Boulder, Colorado
November 11, 1993

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INTRODUCTION

Phase I of the NASA High-Speed Research Program (HSRP) is scheduled to be completed in September 1995. At that time, the Atmospheric Effects of Stratospheric Aircraft (AESA) component of HSRP is required to produce a final Phase I assessment of the potential impact of a fleet of high-speed civil transport (HSCT) aircraft. AESA recently completed an interim assessment, NASA Reference Publication 1333, which was submitted to the National Research Council Panel on Atmospheric Effects of Stratospheric Aircraft for review.

The models used for the interim assessment were basically those described in the Models and Measurements (M&M) Workshop report, NASA Reference Publication 1292. This and other model intercomparison efforts have revealed that discrepancies still exist in the results of different assessment models, particularly in the calculated photolysis rates, treatment of diurnal species, and transport fluxes. Comparison of model results with observations also reveals areas of discrepancy; in particular, most assessment models do not reproduce the apparent transport barriers deduced from trace constituent gradients near the polar vortices and subtropical jets. Finally, continued laboratory work on heterogeneous reactions indicates that the dependence of certain heterogeneous processes on temperature, composition, and size distribution may not be fully accounted for in assessment models.

In preparation for the 1995 assessment, a process has been started to further intercompare and improve participating models. As a first step in this process, the Assessment Model Workshop was held on November 11, 1993, in Boulder, Colorado, to discuss possible ways in which the above model discrepancies/deficiencies could be resolved. The workshop had the following specific goals:

- To review salient areas of discrepancy in model-model and model-data comparison
- To discuss model parameterizations and future intercomparison exercises which could lead to improvements in existing discrepancies
- To prioritize areas in which improvements and/or intercomparisons could be carried out in time for the 1995 assessment

The purpose of this chapter is to provide a summary of the presentations and conclusions of this workshop. As such, it must be considered work in progress. A continuation of this effort is being carried out, with further workshops planned to address specific goals and tasks. The sections that follow summarize results presented under each section of the workshop.

SUMMARY OF PREVIOUS MODEL-MODEL AND MODEL-DATA INTER-COMPARISONS

The purpose of this section was to review the current status of model-model and model-data intercomparison, in order to set the stage for discussing future efforts.

Presenter: E. Remsberg, NASA/Langley Research Center

This presentation served as a "roadmap" through the report from the M&M Workshop, held in February 1992, in Satellite Beach, Florida. Fourteen modeling groups participated in that effort. The experiments were designed to test different aspects of model transport, radiation, and photochemistry. The effort also provided comparisons between model results, measured profiles, and column concentrations of trace species and between the correlation of trace species, calculated by models, to those obtained from observations.

Details of the calculations and results are provided in NASA Reference Publication 1292. Model results and measurements used in the M&M exercise also are available in CD-ROM format.

The following issues were highlighted as being of particular relevance to the goals of this workshop:

- Although photolysis calculations compare better than in previous intercomparisons, there is still a significant discrepancy among results from different groups (on the order of 30 percent or larger), particularly for processes where multiple scattering in the near-UV becomes important
- Ozone loss frequencies calculated by different models at 20 km differ by a factor of two
- Models underpredict ozone at 40 km
- Models also differ in calculated heating rates; these differences are not solely attributable to differences in temperatures
- Calculated distributions of synthetic tracers indicate differences in the transport of different models

The following recommendations were proposed for future intercomparison exercises:

- Limit the focus of the exercises to more detailed cases, while at the same time incorporating relevant results from three-dimensional models
- Utilize relevant data from the Upper Atmosphere Research Satellite (UARS), aircraft campaigns, and other sources to further check model transport
- Derive residence times, based on the observed time dependence, for Mt. Pinatubo aerosols
- Utilize data from ATMOS 1 and ATMOS 2 to further test effects of heterogeneous chemistry
- Utilize the data set from the Stratospheric Photochemistry, Aerosol and Dynamics Expedition (SPADE) for photolysis and chemistry comparisons
- Remodel NO_y/O_3 ratio distributions near the tropopause
- Address interannual variations in transport and NO_y residence times

Presenter: R. Salawitch, Harvard University

Data from aircraft campaigns such as the second Airborne Arctic Stratospheric Experiment (AASE-II) and SPADE provide additional constraints for model results. However, given the difficulties in directly comparing results from a zonally averaged model to *in situ* aircraft observations, intermediate "process" models must be considered to test the mechanisms incorporated into assessment models.

This presentation summarized ongoing efforts on aircraft data analysis, utilizing the air-parcel/photochemistry package developed by different investigators. This model comprises two main components:

1. An air-parcel trajectory model (with coupled radiation and photochemistry). This model complements the steady-state approach described in the next paragraph, particularly for situations where air-parcel trajectories exhibit large, latitudinal excursions. This package integrates modules developed by different investigators addressing the following aspects of the problem: calculation of air-parcel trajectories; calculation of ozone and temperature profiles above the trajectory; derivation of surface and cloud albedo, aerosol optical thickness, and column ozone from satellite observations; calculation of photolysis rates; initialization of trace gas concentrations for the air parcels; aerosol microphysics; and calculation of photochemical time development along air parcels.
2. A steady-state photochemical model. This model uses, as input, measured or reconstructed concentrations of trace species (Salawitch *et al.*, 1994), temperature, pressure, overhead ozone column densities normalized to satellite data, and aerosol surface area concentrations derived from observations. Concentrations of short-lived species are then calculated, assuming that air-parcel motion is along a fixed latitude and height.

Preliminary comparisons indicate that the HCl concentrations, measured during SPADE and AASE-II, are still about 50 percent lower than calculations which include heterogeneous chemistry. The model is also being used to examine NO_x/NO_y and ClO/Cl_y partitioning for different assumptions about heterogeneous chemistry.

IMPROVING (PHOTOLYTIC) RADIATIVE PARAMETERIZATIONS: POTENTIAL REFERENCE MODELS

Presenter: R. Kawa, NASA/Goddard Space Flight Center

The M&M exercise indicated that significant discrepancies (i.e., 30 percent or greater) still existed among photolysis rates calculated by different models for a prescribed atmosphere. Discrepancies were noted even for calculations which did not include multiple scattering of radiation.

The presentation proposed a possible blueprint for future efforts towards resolution of this problem. This includes the following two elements:

1. Determination of modeling experiments and diagnostics, which would test specific areas of discrepancy in models
2. Providing modelers with a set of diagnostics, from one or two "standard" models, for the purposes of identifying and resolving discrepancies

Two models, using radiative codes developed by M. J. Prather (University of California, Irvine – UCI) and D. E. Anderson (Applied Physics Laboratory [APL], Johns Hopkins University) were proposed to provide the above yardsticks for comparison. The UCI code was developed as one of the modules for the air parcel model discussed above. Wavelength resolution in this code has been optimized for computational efficiency. The APL code, with high wavelength resolution, has been utilized in the analysis of high solar zenith angle observations by the polar aircraft campaigns. Both codes include parameterizations for Rayleigh scattering, absorption in the Schumann-Runge region, and aerosol scattering.

Results from these models were compared for the following three experiments:

- "Molecular multiple scattering" experiment. This calculation concentrated on the altitude profile of the radiative source function at 400 nm. Calculations by the two models were in good agreement with each other for different solar zenith angles and albedos.
- "Absorption/scattering/photolysis" experiment. Comparisons of the radiative source function from 175 to 850 nm were presented at different pressure levels and solar zenith angles. Photolysis rates for several important atmospheric processes were also presented. Overall, results from both models compared well (Figure 1). The largest differences between the two models were found in the photolysis and quantum yield of NO₃, the photolysis of N₂O₅, and the photolysis of ozone in the O(¹D) channel at solar zenith angles larger than 80° in the troposphere/lower stratosphere. These discrepancies are due primarily to differences in adopted cross sections, quantum yields, and their temperature dependencies, rather than to differences in radiative calculations.
- "Aerosol scattering" experiment. The models calculated the radiative effects of large volcanic eruption by introducing a sulfate/solid aerosol layer peaking at 19 km, with a total extinction optical depth of 0.39. Calculations from both models indicate that the impact of such a layer would become important only at solar zenith angles greater than 80°, below an altitude of 60 mb (Figure 2).

After this presentation, the participants concurred that in an effort towards improving assessment models, the resolution of photolysis discrepancies were of the highest priority. It was suggested that the results and diagnostics from the above models, for specific experiments, be provided to workshop participants as part of the database collected by the Upper Atmosphere Data Program.

IMPROVING PARAMETERIZATIONS OF HETEROGENEOUS CHEMISTRY

Presenter: A. R. Ravishankara, National Oceanic and Atmospheric Administration (NOAA)/Aeronomy Lab

Summary of results from the heterogeneous chemistry workshop. This presentation summarized results from the heterogeneous chemistry workshop, which took place from November 8-10, 1993, in Boulder, Colorado (see Chapter 3 of this report). Emphasis was on results of direct relevance to the hypersonic civil transport issue. The presentations and discussions at the heterogeneous chemistry workshop dealt with two general categories: microphysics and observations of stratospheric particles, such as sulfate aerosols and Polar Stratospheric Clouds (PSCs) with regard to information on their surface area, volume, number, and composition; and reactivity of specified surfaces in the laboratory and the applicability of these measurements to the atmosphere.

Polar Stratospheric Clouds. Surface area, number, location, duration, and time of year.

- We are not in a position to accurately predict the above PSC parameters from microphysics
- Satellite (e.g., Stratospheric Aerosol Measurements II [SAM-II]) climatology is robust, and the possibility of empirically predicting the surface area of PSCs from temperature should be investigated
- Composition of PSCs is unclear from observations, laboratory studies, and microphysics

Sulfate Aerosols. Surface area and composition.

- The above parameters are determined "almost exclusively" by the frequency of volcanic eruptions. It is not clear how "clean" the stratosphere can get between eruptions
- The composition changes with temperature and partial pressure of water and nitric acid, as predicted by thermodynamics
- The phase of the aerosol (solid or liquid) is unclear in the temperature range from 189 K to 220 K. The phase may depend on the history of the particle (i. e., whether it was previously frozen in a PSC)

Reactivity on Polar Stratospheric Clouds

- Given the fast rate of many heterogeneous reactions on PSCs, details of the microphysics and reactivity may not matter.
- Laboratory studies have shown that:
 - Reactions of N_2O_5 and ClONO_2 with H_2O are fast on ice, but slow on nitric acid trihydrate (NAT). Furthermore, rates for these reactions are independent of relative humidity
 - Reactions of ClONO_2 and HOCl with HCl are fast on ice and fast on NAT, but depend on relative humidity
 - The reaction of N_2O_5 with HCl is not well studied, but it is unlikely to be fast on NAT
- The processes which determine denitrification, via PSC formation, are not well understood. This is a crucial gap in our knowledge.

Reactivity on Sulfate Aerosols

- $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$: This reaction is fast on supercooled aerosols, with rates independent of temperature and relative humidity. The reaction is slow on frozen aerosols.
- $\text{ClONO}_2 + \text{H}_2\text{O}$: The rate is a function of the weight percent of sulfuric acid in supercooled aerosols. Parameterizations based on laboratory data are now available. The reaction is slow on frozen sulfate aerosols.
- $\text{ClONO}_2 + \text{HCl}$ and $\text{HOCl} + \text{HCl}$: The rate is a function of the weight percent of sulfuric acid in supercooled aerosols. Parameterizations are also available. These reactions are fast on frozen aerosols, with rates a function of relative humidity.

Assessment Tactics and Issues

- Since PSC processes are fast, there is no need to worry about details of PSC formation and composition; modelers can use the SAM-II climatology for surface area. Denitrification, however, is an area of crucial importance which we do not know how to address.
- At mid-latitudes, temperatures are high enough that reactions involving HCl on sulfate aerosols are not important. The measured rate for $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$, and the parameterization for $\text{ClONO}_2 + \text{H}_2\text{O}$ should be used.

- Since we cannot predict, with confidence, the sulfate loading for different conditions, assessment efforts should use "prescribed" sulfate loadings (e.g., background conditions, volcanic conditions, average conditions).
- Reaction rate constants on sulfate aerosols, at temperatures between 190 K and 215 K, represent an area of great uncertainty. Modelers should also include the reactions of ClONO_2 and HOCl with HCl , using the available parameterizations (Hanson *et al.*, 1994). These parameterizations may have to be modified for temperature fluctuations, along a latitude band through appropriate, off-line calculations.

Presenter: D. Considine, NASA/Goddard Space Flight Center

Parameterization of PSCs for two-dimensional photochemical models. PSCs, both NAT and ice, develop when the temperature reaches a "formation" temperature, T_c . This temperature may correspond to the saturation temperature, or it may be two to three degrees below T_c , if significant supersaturation is required before PSCs will condense. Two-dimensional models, which use zonally-averaged temperatures, may misrepresent formation of PSCs along a latitude band due to temperature fluctuations about the zonal mean.

The work presented a parameterization of PSC formation which could be used to assess the potential impact of PSC formation in an assessment of HSCT aircraft. The goals of this parameterization are realistic behavior of PSCs for a present-day, base case; response to perturbations due, for example, to increases in NO_x due to HSCTs; and, simple to incorporate into two-dimensional models (no microphysics).

The basic approach of this parameterization is as follows:

- Statistics from a temperature climatology are used to derive a probability distribution, $P(T)$, as a function of latitude and pressure. Integration of $P(T)$ up to T_c , yields the saturation fraction, f , as a function of latitude. This parameter corresponds to the fraction of a latitudinal band whose temperatures are below the saturation temperature for NAT/ice. In the work presented, the National Meteorological Center analysis (from 1989-1992) was used to derive the above statistics.
- A log-normal size distribution of NAT and ice PSCs is assumed. The size distribution is used to calculate the relationship between PSC volume and surface area. The volume of NAT, for instance, is then calculated at a particular latitude and pressure level by integrating $\{[\text{HNO}_3](\text{ambient}) - [\text{HNO}_3](\text{sat})\}P(T)$ up to T_c , where $\text{HNO}_3(\text{sat})$ is the saturation vapor pressure nitric acid over NAT. We then assume that this difference is incorporated into NATs. The same procedure is used for ice PSCs.
- Heterogeneous chemistry on PSCs is incorporated at each model gridpoint assuming derived, average, PSC area concentrations.

Preliminary calculations of the saturation fraction and PSC surface area density, as a function of latitude, were presented for 1990 conditions. Incorporation of these preliminary calculations into the NASA/Goddard, two-dimensional model yielded the following:

- Ozone columns for 1990 conditions decreased by about two percent in the tropics. Northern Hemisphere column ozone was reduced by up to 10 percent at high latitudes in late spring. Southern Hemisphere column reductions of over 50 percent occur in the late spring at high latitudes, when compared to a non-PSC run. The PSC parameterization thus produces a feature in column ozone which resembles the stratospheric ozone hole.

- Inclusion of PSCs produced small changes (i.e., approximately 10-percent reductions) in model predictions of the HSCT impact on column ozone from those calculated by a model including heterogeneous chemistry only on sulfate aerosols. The impact of the PSCs at mid-latitudes, on the relative importance of the different loss cycles, is similar to that produced by sulfate aerosols. These changes decrease model sensitivity to HSCTs. The increased PSC processing that results from increased PSC occurrence, when the HSCTs are added, is generally not large enough to counter this effect. An exception occurs at Southern Hemisphere high latitudes in late spring, where increases in PSC surface area density result in larger, column ozone reductions.

Further sensitivity studies are needed to determine the response of the parameterizations to different assumptions about temperature statistics, PSC formation parameters, and heterogeneous chemistry parameterization.

IMPROVING TRANSPORT PARAMETERIZATIONS

Two-dimensional assessment models have not been able to reproduce certain features observed in satellite and aircraft measurements. Such features include apparent barriers to transport across the polar vortices and subtropical jets, vertical descent at high latitudes, and vertical profiles of trace species at high latitudes. Recent formulations of transport in two-dimensional models have begun to yield more realistic results in the above regions.

Presenter: R. Garcia, National Center for Atmospheric Research (NCAR)

Numerical model of the middle atmosphere. Results were presented from an updated formulation of the NCAR/NOAA, two-dimensional model. This formulation has been described in Garcia (1991), Garcia *et al.* (1992), and Garcia and Solomon (1994). The main features of this updated model are:

- Transformed Eulerian Mean formulation
- Altitude domain from 2 km to 112 km
- Parameterization of gravity wave breaking
- Explicit calculation of single ($k=1$) planetary wave
- Planetary wave-breaking parameterization
- Infrared cooling from the CCM2 model, for $z < 70$ km
- Semi-Lagrangian transport of trace species

The parameterization of planetary wave breaking, in particular, allows calculation of the horizontal eddy coefficient K_{yy} in a manner analogous to the calculation of K_{zz} from the breaking of gravity waves (i.e., by balancing wave activity flux with dissipation due to wave breaking). Propagation of planetary waves is considered in both vertical and horizontal directions.

Implementation of the above parameterizations yields the following improvements:

- Decreased mixing across the polar vortex as indicated by sharper gradients in mixing surfaces

- Maximum descent at vortex edge
- Calculated N₂O distribution in the subtropics in better agreement with UARS observations (Randel *et al.*, 1993), indicating some reduction in horizontal mixing
- Better agreement between calculated altitude profiles for N₂O at high latitudes and measurements from the aircraft polar campaigns
- Consistency between calculated seasonal and latitudinal distribution of column ozone and observations by the Total Ozone Mapping Spectrometer

Presenter: K. K. Tung, University of Washington

A diagnostic approach has been followed in other two-dimensional models (Yang *et al.*, 1991). Fields of temperature and Ertel's potential vorticity, derived from existing analysis of observations, are used to derive heating rates and Eliassen-Palm (EP) fluxes, from which self-consistent residual circulation velocities and K_{yy} can be derived.

A simpler fix to the transport parameterization was proposed by this presentation. This fix assumes that eddy coefficients are diagnosed from EP flux divergences. A Rayleigh friction term is added to the dissipation term at high latitudes, thus reducing K_{yy} in the polar regions.

Outstanding Issues/Ongoing Work

- Role of synoptic-scale wave breaking in the lower stratosphere
- Processes determining tropical ozone columns
- Transport of water across the tropopause
- Characteristics of transport barrier across the subtropical jet
- Application of semi-Lagrangian methods in transport modules
- Development and utilization of transport diagnostics for model intercomparison

ONGOING EFFORTS AT MODEL INTERCOMPARISON

**Presenters: M. Ko, Atmospheric and Environmental Research, Inc. (AER)
C. Jackman, NASA/Goddard Space Flight Center**

Results from the last interim assessment indicate that, although model results have continued to converge, there is still a considerable spread in the calculated response of NO_y and ozone to a prescribed HSCT injection of NO_x. This situation points to the need for further model intercomparison.

Previous intercomparison efforts have involved many modeling groups entailing analysis of a large number of data sets and precluding detailed analysis of areas of discrepancy. Another approach is to have two modeling groups engage in a detailed intercomparison of certain model results. Areas of improvement and suggested modifications arising from this intercomparison can then be transmitted to other groups prior to intercomparison/assessment exercises involving all models.

The AER and NASA/Goddard groups have started a prototype intercomparison exercise of their model results. The motivations for this exercise are to ensure that differences in model results are due to differences in approach or input, and not to error; analyze results more critically; c) isolate the chemistry in the model for intercomparison; and, isolate differences due to transport.

Two specific experiments have been started:

1. Baseline case – for fixed profiles of O_3 , H_2O , NO_y , HNO_3 , Cl_y , Br_y , and CH_4 – models calculate production and loss of ozone.
Preliminary results: For March, $60^\circ N$, there are significant discrepancies in the calculated production of odd oxygen by photolysis of O_2 , pointing to the need for intercomparison of radiative codes. Calculated ozone production in the troposphere from the smog reactions are also different.
2. Perturbation case – for input ΔNO_y and ΔH_2O – models calculate new P and L and compare ΔP and ΔL .
Results: The decision was made to input the ΔNO_y as NO_x , keeping HNO_3 fixed. This resulted in non-realistic partitioning of the species in the NO_x family. The calculated changes in loss frequencies for both models are again different. However, this exercise should be repeated by letting both NO_x and HNO_3 respond to the HSCT perturbation.

SUMMARY AND ACTION ITEMS

Presenters: R. Stolarski, NASA/Goddard Space Flight Center
J. Rodriguez, Atmospheric and Environmental Research, Inc. (AER)

Steps in Model Intercomparison:

- Radiation. The following should be intercompared:
 - Cross sections
 - Schumann-Runge band parameterization
 - Reduced flux, as a function of altitude
 - Partial contributions to photolysis rates, by each wavelength interval ($dJ/d\lambda$)
- Chemistry:
 - Specify tracers -> Calculate chemistry -> Specify ΔNO_y -> Recalculate chemistry -> Compare and analyze sensitivity to different parameterizations

Also, it would be very useful for each model to compare the results of their chemical packages to the photochemical calculations performed by the trajectory model. This could be achieved, for example, by models running a given trajectory with their own chemistry and radiation.

- Dynamics:
 - Can we define a direct intercomparison?
 - Carry out sensitivity studies of ΔO_3 , ΔNO_y , and ΔH_2O in response to a given HSCT emission, as a function of transport parameters. Examine the impact of improved planetary wave-breaking parameterization and heating rate calculations.
 - Utilize three-dimensional simulations to estimate the importance of synoptic scale events.

1995 Aircraft Assessment: Possible Elements

- Assess basic cases with several improved models. Perturbations in NO_x , H_2O , CO , CH_4 , for an emissions index of NO_x of 2, 5, and 15, at Mach 1.6, 2.0, and 2.4
- Test known parameter space in order to evaluate uncertainties and confidence in the results. Possible parameters include:
 - Model formulations: wave parameterization, heating rates, tropospheric dynamics, rainout, and lightning sources
 - Model input: altitude and latitude of injection, emission index, Cl_x amount, reaction rates (both gas and heterogeneous), cross sections, boundary conditions, and tropospheric chemistry
 - Microphysics parameters: saturation temperature of NAT or ice, denitrification assumptions, and sulfate aerosol composition and concentrations
- Evaluate other effects, either by model calculations or estimates, including soot, new particle formation, and organic hydrocarbon emissions
- Identify and assess potential climate effects due to changes in ozone, water, and/or particles

Action Items: (To be carried out and tested by December 1994)

- Detailed comparison of diagnostics of radiative codes with those from the UCI and APL models (Effort coordinated by R. Kawa)
- Implement parameterization for heterogeneous chemistry on sulfate aerosols for reactions of $\text{ClNO}_3 + \text{H}_2\text{O}$; $\text{ClNO}_3 + \text{HCl}$; $\text{HOCl} + \text{HCl}$; and $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ (Parameterizations provided by A. R. Ravishankara)
- Implement wave-breaking parameterization (R. Garcia) or Rayleigh friction "quick fix" (K. K. Tung)
- Define and carry out sensitivity/uncertainty and intercomparison analysis cases for:
 - Chemistry: Coordinators, M. Ko and C. Jackman
 - Dynamics: Coordinators, K. K. Tung and C. Jackman
 - Sulfate loading: Coordinator, A. R. Ravishankara
 - PSC parameterization: Coordinator, D. Considine
 - Temperature fluctuations

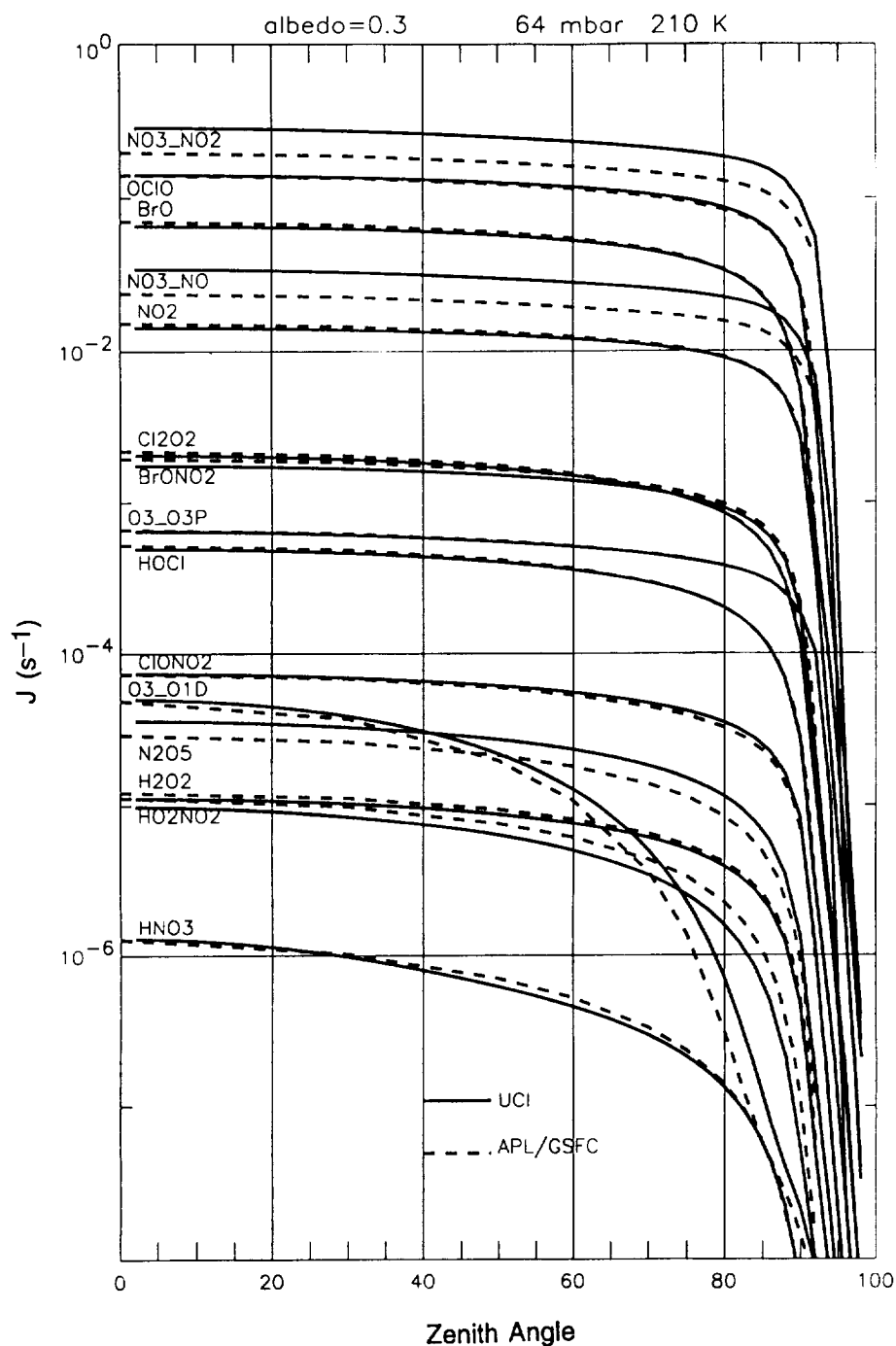


Figure 1. Comparison of photolysis rates as a function of solar zenith angle for a variety of species. The UCI curves use calculations from the model of M. J. Prather (University of California, Irvine) while the APL/GSFC curves use radiative transfer calculations from D. E. Anderson (Applied Physics Laboratory, Johns Hopkins University) with cross section and wavelength integration from the NASA Goddard 3-D model. Rates are plotted at 64 mbar, 210 K for clear sky conditions and a surface albedo of 0.3. The total ozone column is about 325 DU.

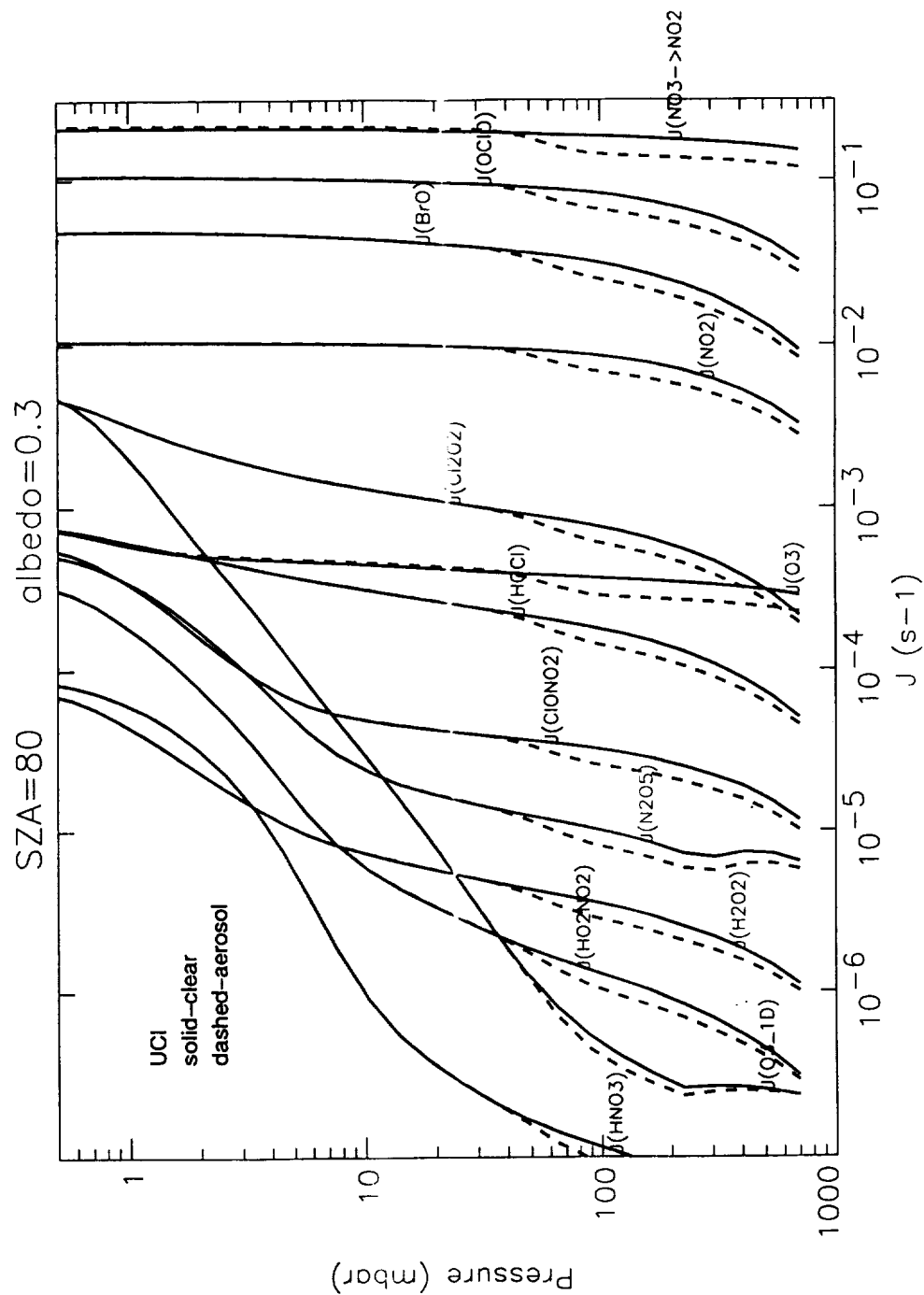


Figure 2. Profiles of photolysis rates as a function of pressure from the UCI model showing the effect of a lower-stratospheric aerosol layer. The aerosol layer was typical of a recent volcanic injection of large magnitude centered near 20 km. Rates are plotted for a solar zenith angle of 80 degrees and a surface albedo of 0.3. Total ozone is about 325 DU.

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Chapter 5

Aircraft Exhaust Plume and Wake Vortex Near-Field Interactions

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INTRODUCTION

This report summarizes the accomplishments of the Atmospheric Effects of Aviation Project (AEAP) near-field interactions program, which was last detailed in the Atmospheric Effects of Stratospheric Aircraft (AESA) Third Program Report (Stolarski and Wesoky, 1993). While most of the AESA effort continues to focus on stratospheric flight conditions, some activities have been initiated to investigate near-field effects for subsonic flight in the upper troposphere in support of the Subsonic Assessment (SASS) program.

The basic goals of the current near-field interaction effort are to:

- Specify the chemical and physical states of aircraft exhaust species in current and prospective air traffic corridors, over spatial scales consistent with the input requirements of atmospheric impact assessment models
- Predict the chemical and physical properties of exhaust/atmospheric flow regimes behind aircraft, so that potential AEAP wind tunnel or flight experiments to probe these regimes can be systematically evaluated
- Provide a set of computational tools to analyze data from exhaust/atmospheric flow regime wind tunnel or flight experiments, sponsored by AEAP or other programs

As described in the AESA Third Program Report, Chapter 6, "Exhaust Plume/Aircraft Wake Vortex Interaction Committee Report," the primary focus of the near-field interactions effort is to assemble and utilize an integrated set of computer models which describe the fluid dynamic, chemical kinetic, condensation and, where appropriate, radiative transfer processes, beginning at the aircraft exhaust nozzle exit plane. These models will incorporate the physical phenomena behind the aircraft for sufficient distances/times that the chemical and physical processes in the exhaust laden air masses can be adequately described with existing atmospheric simulation models. To date, the AEAP near-field interaction effort has not included dedicated wind tunnel or flight experiments specifically designed to measure the chemical and/or physical properties of the atmospheric/exhaust flows behind aircraft. Such experiments could test the suite of computer codes assembled to describe near-field effects in future studies, and some effort has been made already to evaluate remote sensing technologies which might be useful for this type of experiment (Stolarski and Wesoky, 1988). However, some flight data on the chemical evolution of exhaust species and contrail structure behind commercial subsonic aircraft has been gathered (Arnold *et al.*, 1992; Schumann, 1993). Additionally, data on the chemical speciation and condensation nuclei loading of the exhaust behind NASA's ER-2 aircraft has been acquired during AEAP sponsored stratospheric measurement missions (Fahey *et al.*, 1994). These data provide a means for initial evaluation of the current near-field interaction codes for application to aircraft during cruise conditions.

The complex region behind a high altitude aircraft in the upper troposphere or lower stratosphere can be subdivided into, and modeled as, several characteristic, but interconnected, regimes. These include the exhaust jet plume behind each engine nozzle; the wake vortices shed from each wing, which entrain the exhaust plumes at characteristic distances behind the aircraft; the wake vortex break-up region; and an exhaust/atmospheric mixing region in which the exhaust gases are gradually diluted to near-atmospheric levels. Within each of these regimes, it is important to track a number of important chemical and physical properties of the exhaust/atmospheric flows. These properties include the speciation of key reactive chemical families emitted in the exhaust including nitrogen oxides (NO_y), sulfur oxides (SO_x), and hydrogen oxides (HO_x), as well as relatively unreactive exhaust components such as carbon dioxide, carbon monoxide, water vapor, and soot. In addition, models must track the temperature and degree of

dilution of the exhaust, since these properties greatly effect contrail formation and other condensation phenomena behind the aircraft which, in turn, can affect the heterogeneous chemistry and radiative properties of the near-field interaction regimes. Exhaust plume/wake condensation phenomena are complex and can include activation of, and heterogeneous condensation on, soot particles and binary homogeneous nucleation of sulfuric acid and water vapors. A discussion of the rationale for tracking the chemical and condensation related properties can be found in Miake-Lye *et al.* (1993a), as well as in Chapter 6 of the third AESA program report. The basic approach to modeling each of these regimes was discussed in the third AESA program report. The current report will document: upgrades to the models being developed under this program; progress in integrating and testing the models; and, initial utilization of the models to analyze available flight data.

FLOWFIELD MODELING

Initialization

The fluid dynamical processes in the wake of aircraft define the mixing environment in which chemical and physical processes proceed. Initial, rapid mixing occurs in the engine jet flowfield, which continues to be modeled using the SPF-2 plume flow code, as reported earlier (Stolarski and Wesoky, 1993; Miake-Lye *et al.*, 1993a,b). The inputs to the plume calculation are based on estimates of engine performance from the engine manufacturers or through the Engine Exhaust Trace Chemistry Committee's work. For reactive gases and radicals, which change rapidly near the end of the engine and possibly play a significant role early in the plume, one-dimensional calculations of their chemistry in the engine tailpipe are performed.

These one-dimensional engine exhaust system calculations follow the prescription used in modeling the HSCT engine (Miake-Lye *et al.*, 1993a). In addition to the HSCT engine concept, the Pratt & Whitney J75 engine that powers the ER-2 has been modeled using this approach. In lieu of measurements for these reactive and radical species, one-dimensional calculations can provide physically plausible estimates for levels of OH and CO, in particular, but the detailed engine configuration and non-uniformities in the flow properties cannot be captured in such a calculation. More physically representative calculations will require a higher-dimensional flow model that includes the details of the hot section flow and the passive chemical kinetics to follow the species of interest. It is anticipated that such a model may be developed in ongoing AEAP activities.

Wake Vortex

The diluting exhaust plume subject to the lift-induced trailing vorticity is being modeled using a specialized version of the UNIWAKE vortex wake analysis code. The baseline code has been modified to include passive chemistry (UNIWAKE/PCHEM) that does not affect the flowfield due to minimal thermal effects and little volumetric dilatation of the trace species (Stolarski and Wesoky, 1993, Quackenbush, *et al.*, 1993). Other completed modifications include the capability to accept SPF-2 plume calculation output as input for the exhaust flow in the wake calculation. Initial test cases for a conceptual HSCT configuration and simple chemistry set have been reported (Stolarski and Wesoky, 1993; Quackenbush, *et al.*, 1993). A completed NO_x concentration field of 250 wingspans behind the ER-2 flying at 18.9 km is displayed in Figure 1. Subsequent comparisons of this calculation with the ER-2 emission data (Fahey *et al.*, 1994) will be conducted to evaluate model performance.

Continuing work on the UNIWAKE code is directed at enhancements to the basic model, as well as some numerical problems identified through the calculations performed to date. The direct computations of the near-wake roll up, the inclusion of non-uniform density effects in the crossflow plane, and the addition of a second-order closure turbulence model are currently being

implemented. An apparent numerical instability in the species transport calculation has been identified, and an artificial damping has been used to derive results from the code in its present form. The cause for the numerical instability is being sought, and modifications to the transport equations are anticipated to eliminate it in future versions of the code.

New initialization procedures permit the use of a thin vortical sheet to initialize the wake, in place of the original analytic Betz roll-up procedure. A wide range of sensitivity studies have been undertaken to assess the grid size requirements for such direct computation of the wake roll up. Comparisons against existing flight test data (Snedeker and Bilanin, 1975) have been made to assess the success of the analysis in resolving the roll up of this sheet. The quantitative results obtained to date have been encouraging. Automated techniques are being put in place to allow for the relaxation of grid density as the calculation progresses.

The major addition to the turbulence model is the inclusion of the full dynamic representation of the Reynolds' stresses, in place of the current algebraic model. The governing equations for the Reynolds' stresses have been formulated in the fourth-order accurate form required in UNIWAKE; implementation and testing are currently underway. Finally, corrections to capture the effect of local temperature depression due to finite Mach number effects in the crossflow plane are being implemented. This correction scheme is being drawn from the work of Shanvanda and Oberkampf (1981) and will be implemented and tested in the final months of the present effort.

Far-Wake Dispersion

The far-wake modeling of the exhaust gases performed to date has examined the post-vortex breakup regime. This regime has been analyzed with a Lagrangian box model to address questions of radiatively driven vertical displacements and of the build up of exhaust emissions in a flight corridor due to the passage of multiple airplanes through a given atmospheric region. The minimal radiative subsidence estimated was reported in the third AESA program report and has subsequently been published (Rodriguez *et al.*, 1994).

GAS PHASE CHEMICAL KINETIC MODELING

Most of the initial gas phase chemical conversion of exhaust species occurs in the plume regime, driven by HO_x radicals emitted from the nozzle and the initial mixing of atmospheric O_3 with the exhaust (Miake-Lye *et al.*, 1993a). A detailed chemical kinetic model capable of predicting the oxidation of plume NO to NO_2 , NO_3 , N_2O_5 and HNO_3 ; and SO_2 to SO_3 and H_2SO_4 has been published and incorporated into the SPF-2 plume model (Miake-Lye *et al.*, 1993a,b). More recently this model has been expanded to include HONO formation and destruction utilizing a recent evaluation of NO_y combustion reactions (Tsang and Herron, 1991). This expanded reaction set has been utilized to predict the effects of plume chemistry on NO_y speciation in the NASA ER-2 exhaust (Fahey *et al.*, 1994). The relatively low level of nozzle exit plane OH predicted for the ER-2's J75 turbine engine led to the model's prediction that only a small fraction of the exhaust NO_x was converted to other NO_y species in the plume. Table 1 shows the changes in ER-2 plume NO_y speciation with distance behind the aircraft.

Full NO_y and SO_x chemistry has also been implemented in the UNIWAKE/PCHEM code with some modifications to allow for the larger number of chemical kinetics equations. Exercising the code for the HSCT wake problem led to the conclusion that the gear-type integrator (LSODE) included in PCHEM is not computationally efficient for this problem. Given the fraction of the calculation devoted to chemical kinetics, a faster solver (based on the SENKIN kinetics code from Sandia National Laboratory) was implemented (Lutz *et al.*, 1987). With these modifications, calculations have been performed for a conceptual HSCT and the ER-2, as well as an initial subsonic commercial aircraft configuration (Boeing B-707). The ER-2 calculations were motivated

by the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) mission measurements of the ER-2's own wake during a plume/wake crossing (see below).

The Lagrangian box model, used to calculate the effects of far-wake dilution, heterogeneous chemistry, and gas-phase photochemistry on far-wake radiative properties (Rodriguez *et al.*, 1993) and multi-wake corridor effects (Miake-Lye *et al.*, 1993c), employs the same chemical kinetic and photochemical parameters utilized in the AER two-dimensional global stratospheric model (Ko *et al.*, 1993).

The essential question in the flight corridor calculations is whether or not there are significant non-uniformities in the chemical and condensation behavior in corridors which occur on scales smaller than global circulation model's grids. Local enhancements of water vapor and NO_y are predicted (Miake-Lye *et al.*, 1993c) that would increase Polar Stratospheric Cloud (PSC) formation probabilities at sub-grid scales by factors of two to four (Peter *et al.*, 1991). The increases of 0.5 ppmv H_2O and 0.8-1.6 ppbv HNO_3 extend for length scales of 500 m and persist for one to five days—long enough for PSC nucleation and for subsequent chlorine activation. These results suggest that sub-grid PSCs could be generated in flight corridors, but that the impact of these possible wake-scale PSCs depends on both temperature fluctuations at these scales and the rate of air entrainment into these regions for processing by the aerosol.

NUCLEATION AND CONDENSATION MODELING

Considerable effort has been expended to explicitly compute nucleation and condensation phenomena explicitly in the plume (SPF-2) and wake vortex (UNIWAKE) flow models. Basic phenomena of interest include activation of nucleation on exhaust soot particles (Miake-Lye *et al.*, 1993a,b, c) and binary homogeneous nucleation of plume/wake water vapor with sulfuric acid vapor produced by oxidation of exhaust SO_2 in the plume/wake flow (Zhao and Turco, 1992; Miake-Lye *et al.*, 1993b). This latter phenomenon requires direct coupling of the chemical kinetic production of $\text{H}_2\text{SO}_4(\text{v})$ with ongoing $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ nucleation.

Binary homogeneous and heterogeneous nucleation mechanisms have been incorporated into flowfield codes for the plume (SPF-2) and wake vortex (UNIWAKE) regimes. However, results indicate that binary heterogeneous nucleation rates for nucleation on exhaust soot particulates (0.1 - 1 micron) are several orders of magnitude smaller than binary homogeneous nucleation rates. In both the near-field and wake regions, gas phase SO_x oxidation chemistry and binary nucleation are coupled and embryo transport is included by treating the embryos as gas-phase species. This is a reasonable approximation since calculations indicate that embryo radii, under typical stratospheric plume conditions, range between 0.3 and 0.7 nautical mile (nm).

Binary homogeneous nucleation rates are computed using classical nucleation theory, as formulated in the work of Flood (1934), Reiss (1950), and Doyle (1961) and as exemplified in the study by Kiang and Stauffer (1973).

Results for an axisymmetric plume for a conceptual Mach 2.4 HSCT at 18 km and a latitude of 85N in midwinter are shown in Figures 2 through 4. Results are shown for several streamlines extending from the plume edge to the plume axis. It should be noted that the initial $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ nuclei produced by this process are quite small (of order 1 nm diameter) and, therefore, will not be detected by current condensation nuclei instruments before they undergo extensive agglomeration.

ANALYSIS OF PLUME/WAKE MEASUREMENTS

The Engine Exhaust/Aircraft Vortex Wake Interaction committee has had several discussions of measurements that could provide useful data for testing and validating AEAP modeling efforts. While a variety of suggestions have been proposed, no support for a dedicated measurement

program has been identified yet. Thus, the originally inadvertent intersection of an ER-2 SPADE campaign flight with its own wake provided an unexpected source of experimental data for comparison with model results, albeit at wake development times of the order of 10 minutes. Thus, the ER-2 wake is in the post-breakup regime, vortex breakup occurring roughly 100 seconds after the airplane has past.

The data collected during this wake encounter sensitized the AEAP community to the possibilities of measuring emission parameters for an aircraft in flight. The potential to quantify a given aircraft's emissions in the field were a topic of discussion at a September 1993 SPADE campaign meeting held in Hyannis, MA. This opportunity for analyzing the chemical speciation and condensation nuclei content of the far wake and for comparing models to field measurements has indicated that at least the CO_2 , NO_x , and NO_y evolution are modeled consistently with their measured values (Fahey *et al.*, 1994).

This initial comparison is encouraging and future comparison opportunities are likely to become available. More ER-2 wake encounter measurements have been obtained in ongoing campaigns. In addition, with the successful measurement of emissions in the wake of the ER-2, quantification of emissions from other aircraft, particularly those in the existing subsonic commercial fleet, appears to be achievable. More definitive tests of plume and wake modeling are possible through measurements closer to the aircraft and more use of available data.

Ongoing extension of plume and wake modeling codes to commercial subsonic transports will allow for (1) comparison of model plume NO_y and SO_x speciation and contrail structure predictions with currently-available measurements (Arnold *et al.*, 1992; Schumann, 1993); and (2) any subsequent flight measurements performed by European Community or AEAP researchers, for which data become available.

SUMMARY

The core activity of the near-field interaction effort is the assembly, testing, and utilization of a suite of computer models to describe the fluid dynamic, chemical kinetic, and condensation processes in the exhaust flow/atmospheric mixing regimes behind the aircraft. In the past year, significant progress has been made in upgrading and coupling the chemical kinetic and nucleation phenomena in the exhaust plume and wake vortex regimes and in exercising the UNIWAKE model for the wake vortex regime of a conceptual HSCT. In addition, these models have been used to help analyze the wake crossing data gathered by the ER-2 during a recent AEAP-sponsored field mission. The code suite is also now being applied to commercial subsonic aircraft of interest to the SASS program.

Table 1. Computed species mole fraction versus axial distance for ER-2
[EI (NO_x) = 2.1]

	100 ft	500 ft	1000 ft	1500 ft	2000 ft
NO	3.11 x 10 ⁻⁰⁶	5.21 x 10 ⁻⁰⁷	2.98 x 10 ⁻⁰⁷	2.21 x 10 ⁻⁰⁷	1.82 x 10 ⁻⁰⁷
NO ₂	3.59 x 10 ⁻⁰⁷	6.33 x 10 ⁻⁰⁸	3.78 x 10 ⁻⁰⁸	2.93 x 10 ⁻⁰⁸	2.48 x 10 ⁻⁰⁸
NO ₃	5.85 x 10 ⁻¹³	5.00 x 10 ⁻¹⁵	2.96 x 10 ⁻¹⁵	2.61 x 10 ⁻¹⁵	2.48 x 10 ⁻¹⁵
N ₂ O ₅	3.63 x 10 ⁻¹¹	6.74 x 10 ⁻¹¹	7.00 x 10 ⁻¹¹	7.09 x 10 ⁻¹¹	7.13 x 10 ⁻¹¹
HNO ₂	6.00 x 10 ⁻⁰⁸	1.43 x 10 ⁻⁰⁸	8.23 x 10 ⁻⁰⁹	6.14 x 10 ⁻⁰⁹	5.05 x 10 ⁻⁰⁹
HNO ₃	1.01 x 10 ⁻⁰⁸	3.62 x 10 ⁻⁰⁹	2.53 x 10 ⁻⁰⁹	2.16 x 10 ⁻⁰⁹	1.97 x 10 ⁻⁰⁹
OH	2.99 x 10 ⁻⁰⁸	8.65 x 10 ⁻¹²	2.06 x 10 ⁻¹³	3.39 x 10 ⁻¹⁴	1.42 x 10 ⁻¹⁴
O ₃	8.35 x 10 ⁻⁰⁷	9.78 x 10 ⁻⁰⁷	9.91 x 10 ⁻⁰⁷	9.95 x 10 ⁻⁰⁷	9.97 x 10 ⁻⁰⁷
SO ₂	1.17 x 10 ⁻⁰⁶	1.98 x 10 ⁻⁰⁷	1/13 x 10 ⁻⁰⁷	8.45 x 10 ⁻⁰⁸	6.95 x 10 ⁻⁰⁸
SO ₃	1.60 x 10 ⁻⁰⁹	2.40 x 10 ⁻¹²	8.53 x 10 ⁻¹⁴	1.45 x 10 ⁻¹⁴	5.54 x 10 ⁻¹⁵
HSO ₃	2.69 x 10 ⁻¹³	6.35 x 10 ⁻¹⁷	9.92 x 10 ⁻¹⁹	1.30 x 10 ⁻¹⁹	4.66 x 10 ⁻²⁰
H ₂ SO ₄	8.61 x 10 ⁻⁰⁸	1.62 x 10 ⁻⁰⁸	9.77 x 10 ⁻⁰⁹	7.58 x 10 ⁻⁰⁹	6.43 x 10 ⁻⁰⁹
NO ₂ /NO	0.12	0.12	0.13	0.13	0.14
NO _x /NO _y	0.980	0.970	0.968	0.967	0.967
H ₂ SO ₄ /SO ₂	0.07	0.082	0.086	0.09	0.093

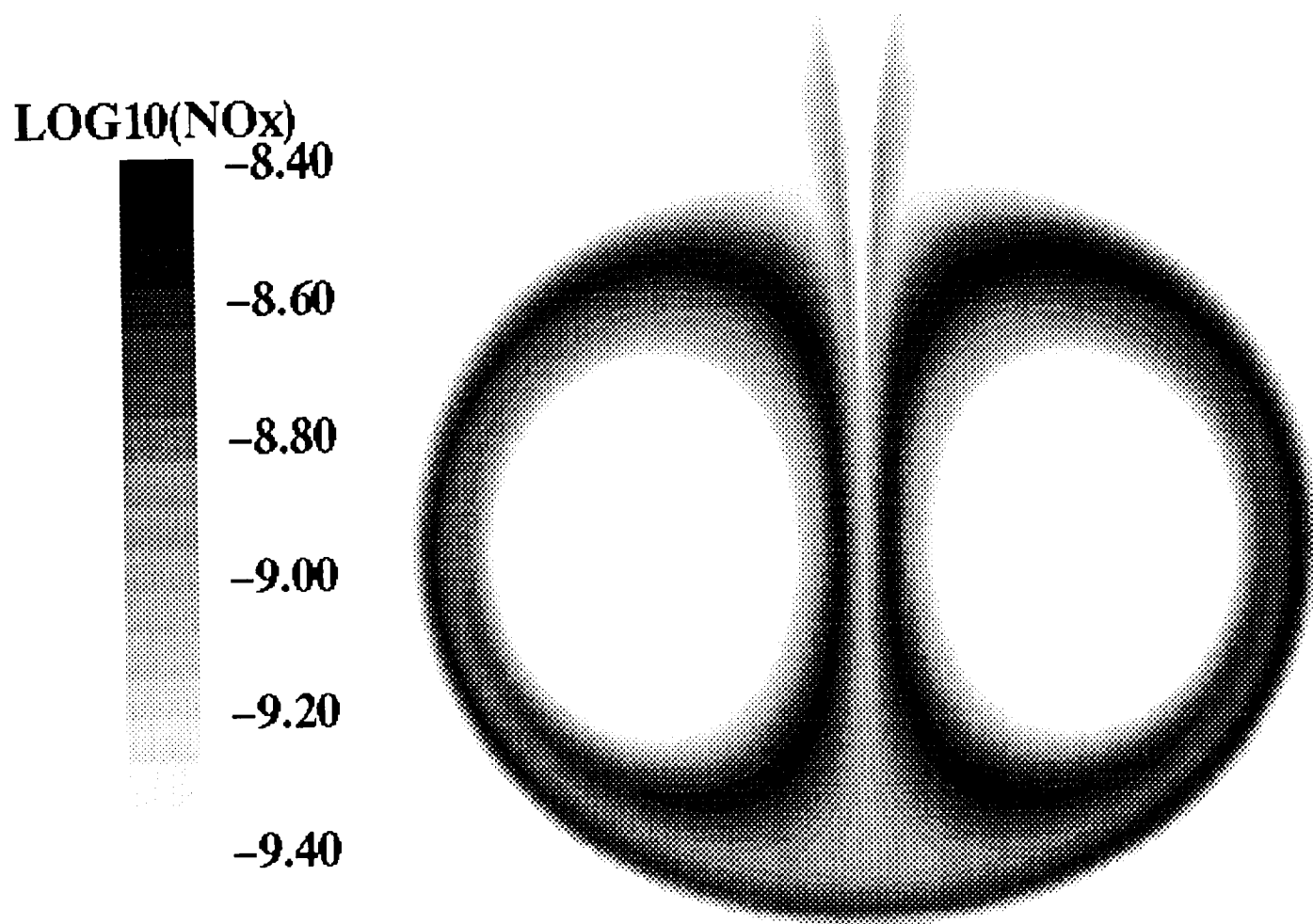


Figure 1. Computed NO_x concentration field (log of NO_x mole fraction) 250 wingspans behind an ER-2 aircraft flying at 18.9 km altitude.

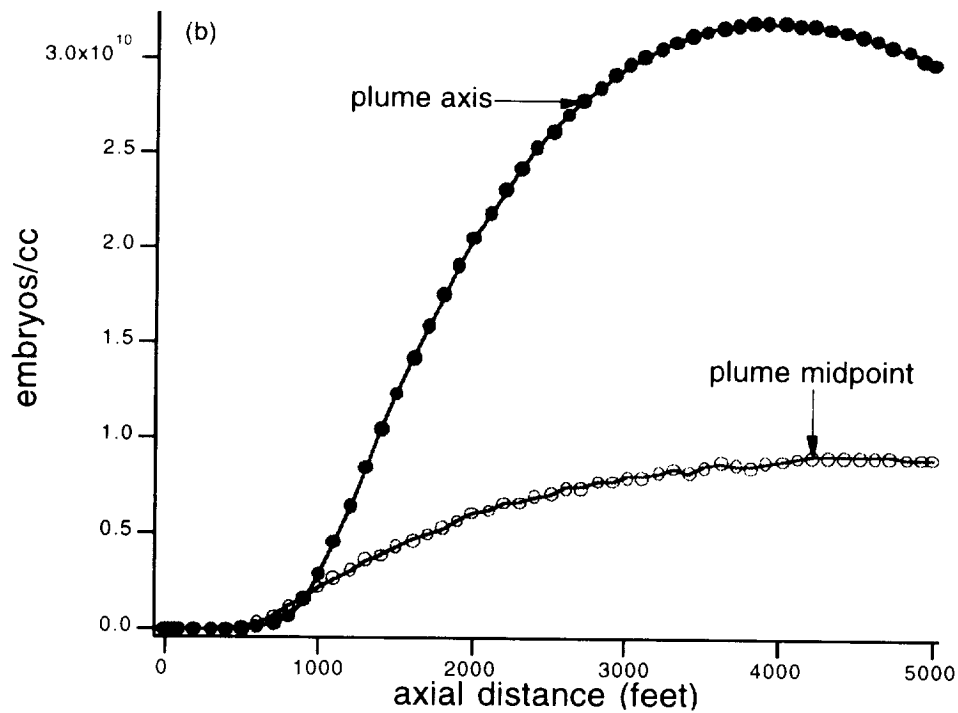
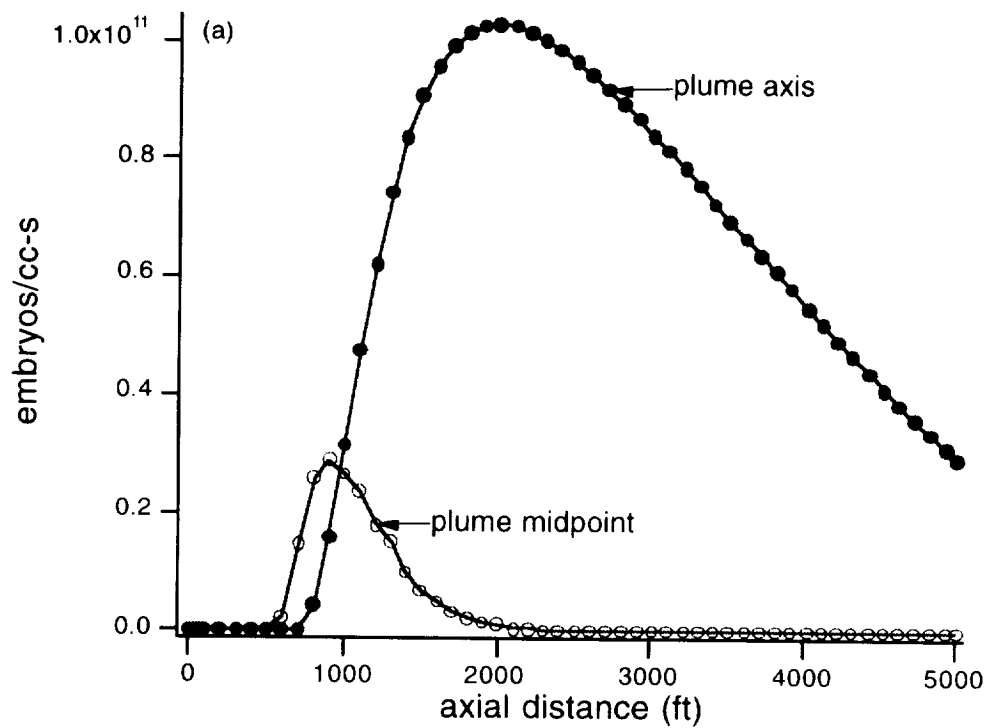


Figure 2. a) Calculated homogeneous nucleation rates, and b) embryo number densities versus axial distance for a Mach 2.4 HSCT at 18 km and a latitude of 85N.

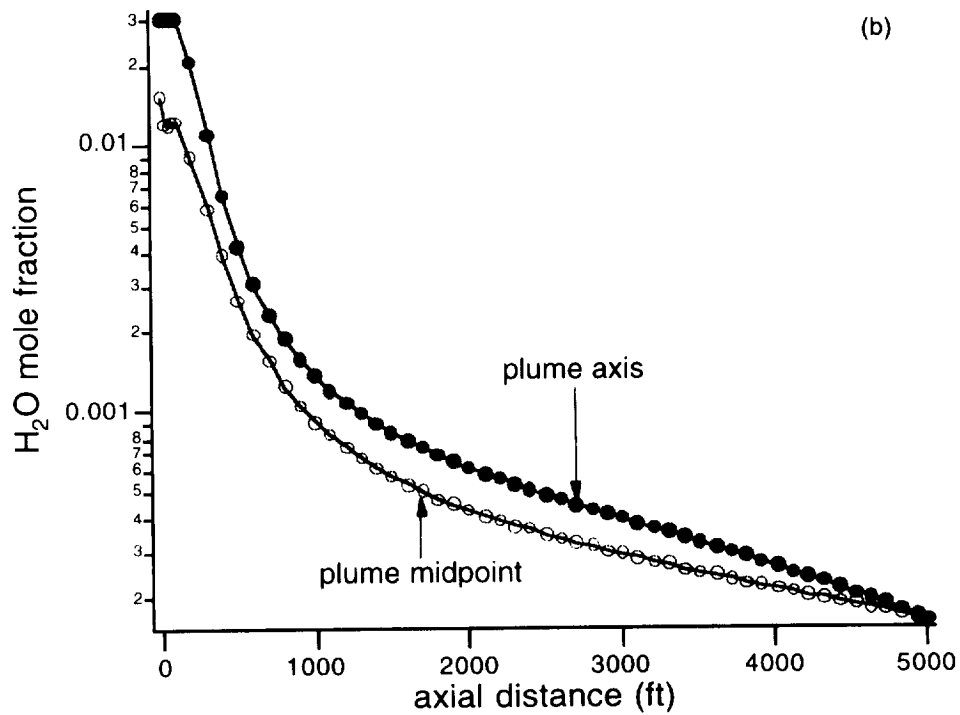
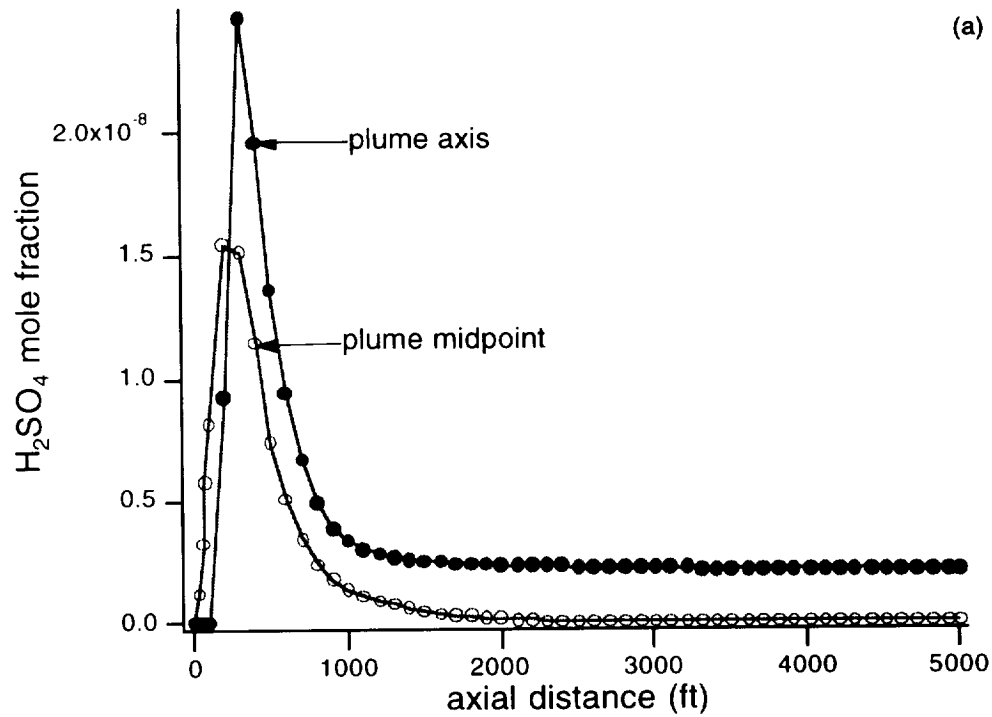


Figure 3. a) Calculated H_2SO_4 , and b) H_2O mole fractions versus axial distance for a Mach 2.4 HSCT at 18 km and a latitude of 85N.

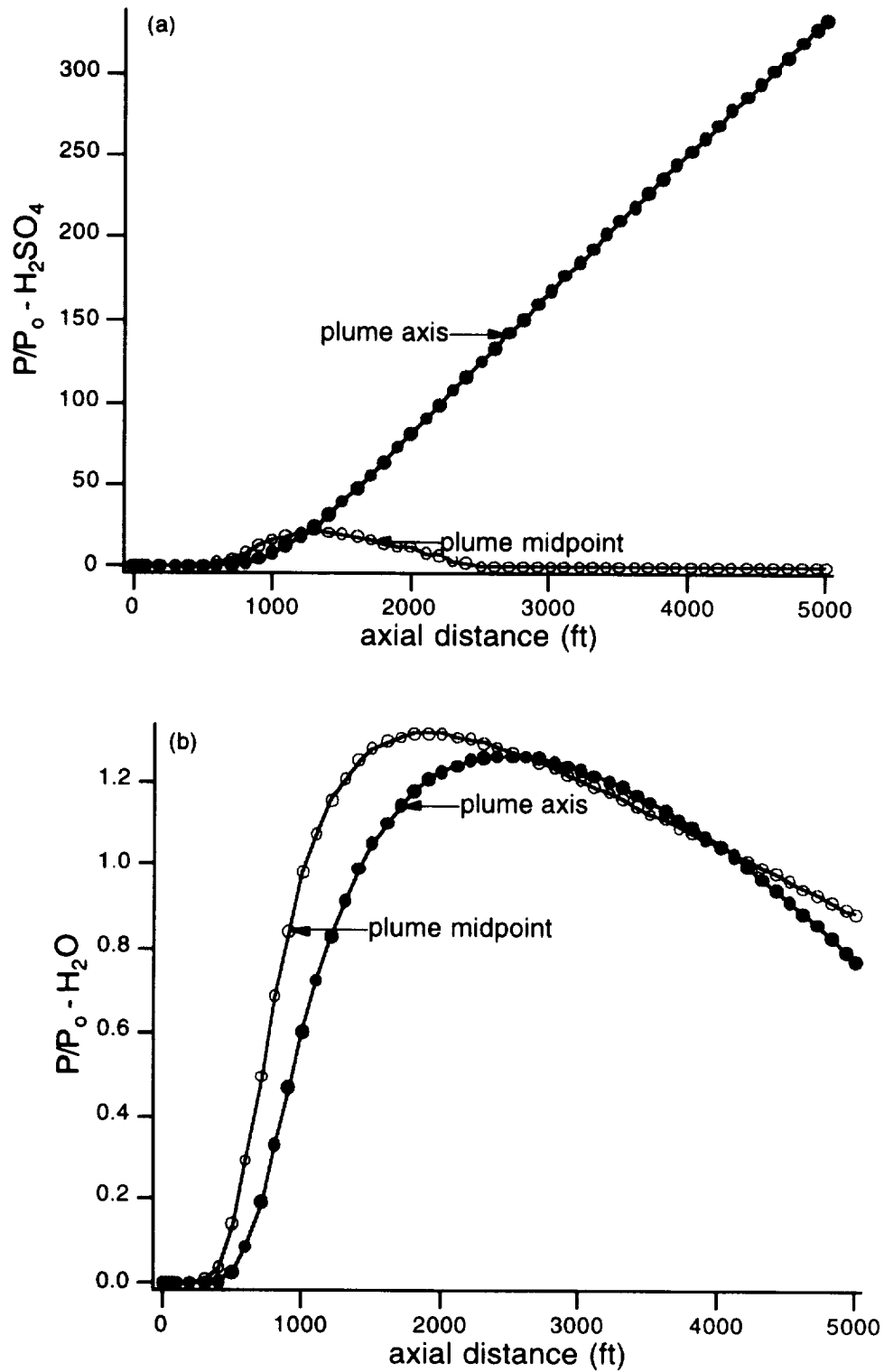


Figure 4. a) Calculated ratio of the vapor pressure to the equilibrium vapor (p) pressure (p_0) for H_2SO_4 , and b) H_2O versus axial distance for a Mach 2.4 HSCT at 18 km and a latitude of 85N.

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Chapter 6

HSRP/AESA Research Summaries

This chapter presents individual summaries of research conducted by investigators supported by High Speed Research Program/Atmospheric Effects of Stratospheric Aircraft. The summaries follow this format: (A) title, (B) investigators and institutions, (C) abstract of research objectives, (D) summary of progress and results to date, and (E) journal publications. These summaries have been edited where necessary. The principal investigator (denoted by an asterisk) is the contact person responsible to HSRP/AESA for the proposed research.

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High Altitude, Tropical Latitude ClO, BrO, O₃, P and T Observations from the Perseus Aircraft for the 1994 ASHOE/SPADE-II Mission

Investigator

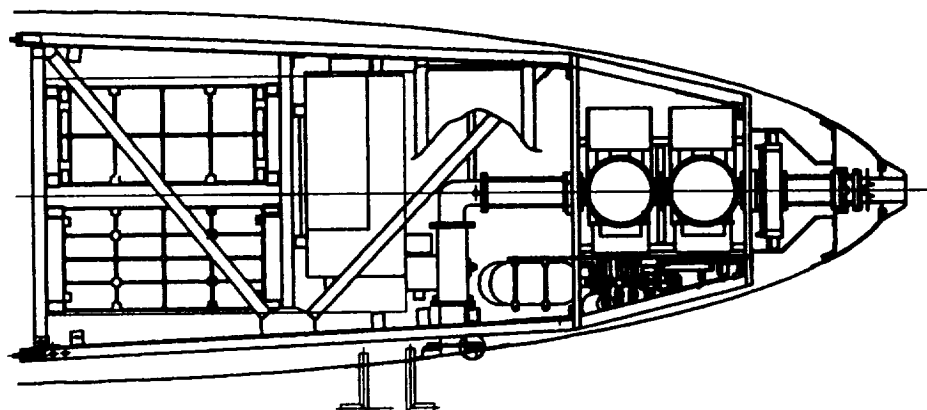
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Research Objectives

The central problem in ozone photochemistry today is to establish the vertical distribution of the rate limiting catalytic steps as a function of altitude, latitude, and season in the region encompassing the preponderance of stratospheric ozone—the altitude region from 20 to 27 km. Unfortunately, to date observations have only been made between altitudes of 16 and 19 km from the ER-2 aircraft, the highest altitude aircraft in the national arsenal. Given the rapid erosion of the total ozone column over mid latitudes of the northern hemisphere, it is essential to pin down the quantitative contributions of the chlorine and bromine catalytic cycles in three key regions: (1) the ozone production zone in the tropics; (2) the "conduit" region that carries ozone poleward and downward; and, (3) the "storage" zone at mid and high latitudes in the lower stratosphere. These observations require flight trajectories approaching 30 km with the ability to cross the subtropical jet and the polar jet. The Perseus aircraft has the ability to satisfy these scientific requirements. Thus, the purpose of this work was the development of a light weight instrument capable of the simultaneous detection of ClO, BrO, O₃, P and temperature. Subsequently, it was decided to add H₂O observations to the companion tracer payload that includes N₂O, CH₄, O₃, and NO_y.

Summary of Progress and Results

There are two phases of this research. Part I involves the development and flight of lightweight ClO, BrO, O₃, P and T instruments suitable for the Perseus RPV or a balloon. Part II involves the development of a Perseus-class payload for flight on the Perseus aircraft. Part I: Balloon profiles of chlorine monoxide (ClO), nitric oxide (NO), and ozone (O₃) were measured on March 11, 1992 from 100 to 10 mb over Greenland (67.0°N, 50.6°W). Measurements from SAGE II indicate that the aerosol surface area in the region was enhanced by sulfur from the eruption of Mt. Pinatubo, reaching 50 times background near 20 km. Concentrations of ClO were enhanced and concentrations of NO were suppressed relative to low aerosol conditions consistent with the effects of hydrolysis of N₂O₅ on the surface of sulfuric acid aerosols. The data are consistent with a value of 2×10^{-4} for the reaction probability of the heterogeneous hydrolysis of ClONO₂, indicating a minor role for this reaction at a temperature of 220 K. At these temperatures, we find no evidence for the catastrophic loss of ozone predicted to occur under conditions of enhanced aerosol surface area. Part II: Development of the Perseus payload has progressed through design, fabrication, and test on schedule. The final design within the Perseus instrument bay nacelle is shown in the adjoining figure. Calibration and test of the instrument is now complete. Flight of the instrument awaits integration onto the aircraft and completion of the aircraft test schedule.



Publications

Dessler, A. E., R. M. Stimpfle, B. C. Daube, R. J. Salawitch, E. M. Weinstock, D. M. Judah, J. D. Burley, J. W. Munger, S. C. Wofsy, J. G. Anderson, M. P. McCormick, and W. P. Chu, Balloon-borne measurements of ClO, NO, and O₃ in a volcanic cloud: An analysis of heterogeneous chemistry between 20 and 30 km, *Geophys. Res. Lett.*, 20, 2527-2530, 1993.

Upgrades to the ER-2 Particle Measurement System

Investigators

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Research Objectives

To replace the ER-2 particle measurement system with a more modern system with greater capabilities.

Summary of Progress and Results

The ER-2 particle measurement system, prior to the upcoming ASHOE mission, consisted of a Focused Cavity Aerosol Spectrometer (FCAS), an FSSP-300, and a Z-80 based data system. This system has been upgraded by replacing the data system with a VME based 68000 series processor recording to a pressure sealed hard drive. The FSSP-300 has been replaced with the new Multiangle Aerosol Spectrometer Probe (MASP) and the FCAS has been improved with state of the art signal processing electronics. The change to the data system added higher rate recording, larger storage space, a larger set of housekeeping variables, and more error recovery code.

The replacement of the FSSP-300 with the MASP has increased the sensitivity to particles down to diameters of almost 0.2 μm , provides additional capability to estimate particle compositions through measurements of the particle index of refraction, and improved the sampling with a more isokinetic inlet. A large number of housekeeping variables are also recorded to monitor the performance of the probe.

The same state-of-the-art signal processing electronics used in the MASP were also installed in the FCAS. This improves the signal to noise ratio and provides much finer resolution than in the original electronics.

The new particle measurement system has now flown on three test flights of the ER-2 during the February pre-ASHOE flights. The preliminary results demonstrated the fundamental robustness of the system and uncalibrated data were taken that showed that the system was working well except for several minor optical adjustment and firmware problems on the MASP processor that have now been corrected.

Publications

None

Enhancements to UNIWAKE to Improve Vortex Wake/Engine Exhaust Dynamics and Chemistry

Investigators

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Research Objectives

The UNIWAKE analysis (Refs. 1 and 2) was originally designed to analyze wing wake evolution for application to the aircraft vortex hazard problem. Recent work under AESA sponsorship extended the capabilities of the baseline code to include passive chemistry as well as tracer trajectory information necessary to assess evaporation and contrail condensation (Refs. 3 and 4) for the HSCT. These tasks produced a derivative of UNIWAKE, denoted UNIWAKE/PCHEM (Passive Chemistry) for application to the analysis of near-field wake/exhaust interaction that is being used by Aerodyne Research, Inc. in support of investigations under the AESA program.

During the current program year, additional features are being incorporated to enhance the applicability of the UNIWAKE/PCHEM to problems of interest in the assessment of both subsonic and supersonic aircraft. The particular technical tasks underway are:

- Enhanced resolution in the near wake rollup model
- Augmentation of the turbulence model to include full dynamic equations
- Addition of compressibility corrections

In addition, ongoing validation tasks have been undertaken to supplement these efforts. The objective of these changes is to bypass significant simplifications in the existing UNIWAKE model and to provide for a more accurate description of the fluid dynamic and thermal environment for wake/exhaust chemistry calculations.

Summary of Progress and Results

New initialization procedures are in place that permit the use of a thin vortical sheet to initialize the wake in place of the original analytic Betz rollup procedure. A wide range of sensitivity studies have been undertaken to assess the grid size requirements for such direct computation of the wake rollup. Comparisons against existing flight test data (Ref. 5) have been made to assess to the success of the analysis in resolving the rollup of this sheet, and the quantitative results obtained to date have been encouraging. Automated techniques are being put in place to allow for the relaxation of grid spacing requirements associated with the thin initial sheet as the calculation progresses.

The major addition to the turbulence model is the inclusion of the full dynamic representation of the Reynolds' stresses in place of the current algebraic model. The governing equations for the Reynolds stresses' have been formulated in the fourth-order accurate form required in UNIWAKE; implementation and testing are currently underway. Finally, corrections to capture the effect of local temperature depression due to finite Mach number effects in the crossflow plane are being implemented. This correction scheme is being drawn from the previous work of Ref. 6 and will be implemented and tested in the final months of the present effort.

Publications

A presentation entitled "Enhancements to the UNIWAKE/PCHEM Wake/Exhaust Mixing Analysis" will be made at the upcoming AEAP meeting that will summarize work on this year's effort. A technical paper that summarizes the results of the present work and extends the discussion of Ref. 4 is also being planned.

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Teske, M. E., T. R. Quackenbush, and A. J. Bilanin, Vortex roll-up, merging, and decay with the UNIWAKE computer program, Proceedings of the FAA International Vortex Wake Symposium, Washington, DC, October 1991.

High-Precision, Fast-Response Instrument for CO₂

Investigators

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Research Objective

The research objective was to obtain further measurements of stratospheric CO₂ from the ER-2 aircraft as a function of season and latitude and to use these results to provide qualitative and quantitative information on troposphere-stratosphere exchange and vertical and quasi-horizontal transport rates in the stratosphere.

Summary of Progress and Results

Because CO₂ in the troposphere varies seasonally on a time scale of a few months, simultaneous measurements of stratospheric CO₂ and N₂O, a long-lived tracer, place strong constraints on transport rates in the lower stratosphere, particularly when data are available from different seasons. Measurements taken during the test flight series of SPADE (November 1992) and the full payload deployment (April/May 1993) were complemented by flying a tracer payload in October 1993 known as the SPADE "micromission." The fact that the correlations between CO₂ and N₂O show very little scatter when simultaneous data points are plotted for each season suggests that meridional mixing is faster than the seasonal CO₂ oscillation, or 2 to 3 months. The observed seasonal dependence of the correlations between these species and their changes from Fall 1992 to Spring 1993 and from Spring 1993 to Fall 1993 indicate that vertical mixing is slower in northern summer than in northern winter above 20 km and slow throughout the year between 19 km and the tropopause. From a comparison with tropospheric CO₂ concentrations from NOAA/CMDL, the mean "age" of the middle stratosphere is approximately 4 to 5 years with "aging" occurring predominantly over the winter indicating that pollutants may accumulate in the lower stratosphere over the northern summer. In addition, the CO₂ concentrations observed and their correlations with the seasonal H₂O mixing ratios suggest that air enters the stratosphere mainly in the tropics. These conclusions are significant for assessing the effect of HSCT's on stratospheric O₃ since each of them affects the residence time and redistribution of HSCT exhaust in the stratosphere.

The total number of flights for the CO₂ instrument for the set of three SPADE deployments is 19. Laboratory and field calibrations as well as in-flight calibrations for each of these flights show that the long-term precision of the ER-2 measurements is +/- 0.04 ppm. A recent inter-comparison of standards with R.F. Keeling at Scripps Institution of Oceanography agrees to better than 0.1 ppm, indicating that the accuracy of the measurements with respect to the Scripps scale is better than +/- 0.1 ppm.

Publications

Boering, K. A., B. C. Daube, Jr., S. C. Wofsy, M. Loewenstein, J. R. Podolske, and E. R. Keim, Tracer-tracer relationships and lower stratospheric dynamics: CO₂ and N₂O correlations during SPADE, *Geophys. Res. Lett.*, 21, 2567-2570, 1994.

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Participation as Mission Scientist for the SPADE II (MAESA) Mission

Investigator

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Research Objectives

Measurements for Assessing the Effects of Stratospheric Aircraft (MAESA) integrates observations from a variety of platforms to gain a better understanding of the effects of a future fleet of stratospheric aircraft. It uses the unique capabilities of the NASA ER-2 high altitude aircraft, with its 17 instruments, to observe the lower stratosphere from 60°N to 65°S. Observations near and in the tropics provide unique data on the mixing and photochemistry of that region. Observations in the southern middle latitudes provide information on low temperature chemical processes and mixing of both tropical and polar air into middle latitudes. Observations of a more limited set of species can be made to altitudes greater than 25 km with either unmanned aircraft or balloons. These measurements are combined with measurements from satellites to both improve and test the models that will be use in the assessment.

Summary of Progress and Results

The Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) began last February with test flights of the NASA ER-2 aircraft at NASA Ames Research Center. These test flights revisited some of the issues during the Stratospheric Photochemistry, Aerosol and Dynamics Experiment. One flight produced a latitudinal profile of species from 37° to 61°N; another produced excellent encounters of the ER-2 with its own exhaust.

The first phase of the four phases of ASHOE/MAESA was completed in mid-April. Successful flights include a transit flight from Moffett Field, California to Barbers Point, Hawaii, three flights from Hawaii toward the tropics, including one that crossed the equator, transit flights from Hawaii to Nadi, Fiji and from Fiji to Christchurch, New Zealand, and 6 flights with two payload configurations from New Zealand, including one flight north.

These flights provide a unique data set because the instruments measure a combination of trace species and meteorological parameters that have never been measured together before from any platform. As a result, each flight provides a new opportunity to learn something new (or confirm something old) about atmospheric chemistry and dynamics. The observations from the test flights and from the first phase of ASHOE/MAESA are now being studied by members of the science team.

Publications

None

Heterogeneous Nucleation Kinetics of Atmospheric Aerosols by Single Particle Measurements in a Quadrupole Trap

Investigators

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Research Objectives

Heterogeneous atmospheric chemistry is a critical issue in assessing the potential effects of stratospheric aircraft. This work is designed to measure physical and chemical properties of single particles under stratospheric conditions in a quadrupole trap. This electrodynamic trap confines the charged particle in an electric field. Particle characteristics including its mass, angularly resolved Mie scattering, and Raman spectrum can be measured as the gas phase composition and temperature are changed.

Summary of Progress and Results

In the second year of this program, we have built a temperature controlled trap facility. Our first studies have examined the freezing behavior of sulfuric acid aerosols. We have cooled 65 wt% sulfuric acid particles to 200 K and observed no freezing. This is 35 K supercooling and supports other observations of the ability of sulfuric acid to supercool. We observe particles for 1 to 3 hours time. Because the nucleation probability is dependent on the particle volume, observation of 20 μm particles for one hour is equivalent to studying 1 μm particles for 8000 hours (~ 1 year). We have modified the apparatus to achieve temperatures of less than 900 K and are extending these freezing studies to the critical 190 to 195 K temperatures regime.

We have completed a preliminary study to examine the hydration properties of model carbon particles. Pure carbon particles are hydrophobic and do not adsorb water as demonstrated by observations of their constant mass in the quadrupole trap as the relative humidity is increased to 80 percent. However, particles which are exposed to sulfuric acid vapor at 140°C do efficiently hydrate. Their hydrate behavior can be modeled based on thermodynamic calculations for the sulfuric acid where the carbon acts as an inert substrate. These particles have a soluble mass fraction of 15 percent which is similar to the 10 percent soluble mass fraction observed for aircraft plume soot particles. This mass fraction corresponds to approximately 0.3 ml of sulfuric acid. This work suggests that the hydration properties of soot can be modified by adsorption of water soluble material. Thus, carbon particles may act as cloud condensation nuclei and are not necessarily inert as has been previously thought.

Publications

Hagen, D. E., M. B. Trueblood, and P. D. Whitefield, A field sampling of jet exhaust aerosols, *Particulate Sci. and Tech.*, 10, 53-63, 1992.

Whitefield, P. D., M. B. Trueblood, and D. E. Hagen, Size and hydration characteristics of laboratory simulated jet engine combustion aerosols, *Particulate Sci. and Tech.*, 11, 25-36, 1992.

Wyslouzil, B., K. L. Carleton, D. Sonnenfroh, W. T. Rawlins, and S. Arnold, Observation of hydration of single, modified carbon aerosols, *Geophys. Res. Lett.*, *21*, 2107-2110, 1994.

The ER-2 Meteorological Measurement System (MMS)

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Research Objectives

- *In situ* measurements of meteorological and state variables (temperature, pressure, winds)
- On-site data analysis and interpretation to enhance the scientific return of a field mission
- Collaborative research in atmospheric dynamics and chemistry

Summary of Progress and Results

All subsystems of the MMS instrumentation were modified in 1992-1994. The following modifications were accomplished in order to improve instrument performance (resolution, computation power) and to reduce weight (from ≈ 206 lb. during AASE-II to ≈ 66 lb. for ASHOE-MAESA).

- Redesign and relocation of the differential pressure system for airflow-angle measurement in order to accommodate a new HO_x instrument in the ER-2 nose.
- Incorporation of the aircraft inertial navigation unit (Litton LTN-92 INS with updating capability from the Global Positioning System) into the MMS configuration in order to reduce science payload weight.
- Development of a new data acquisition system in order to improve computational capability and reduce operational labor.

The MMS participated in the 1992-1993 SPADE mission conducted at Moffett Field, CA. All MMS data were calibrated, reprocessed, distributed and deposited in the archive.

Several times during the 1993 spring SPADE mission, the ER-2 aircraft encountered its own exhaust wake. The ER-2 aircraft flew back and forth at essentially the same altitude, and with a keyhole turn at the end retraced very closely its flight paths. These encounters were observed by fast-response dynamical (pressure, temperature, 3-D winds) and chemical (CO_2 , CNC, H_2O , NO , NO_y) measurements. Preliminary analysis of the data on May 11, 1993 suggests that the trailing vortex after being shed from the ER-2 wings was observed.

Publications

Bowen, S. W., T. P. Bui, K. R. Chan, K. A. Boering, D. W. Fahey, K. K. Kelly, and J. C. Wilson,
A possible ER-2 observation of its own lifting vortex, in preparation.

Assessment of Uncertainties in 2-D Model Predictions of Ozone Depletion Using Restricted Uncertainty Analysis and Sensitivity Studies

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Research Objectives

This research examines the sources and magnitude of uncertainties in 2-D model predictions of HSCT-induced O₃ depletion. The model used in this study is the Goddard Space Flight Center 2-D model, which has participated in the HSRP assessment program. Chemical, radiative, and dynamical uncertainties will be addressed. Radiative and dynamical uncertainties will be addressed using sensitivity studies in conjunction with available measurements. A Monte Carlo uncertainty analysis will be used to evaluate the chemical uncertainties.

Summary of Progress and Results

A parametric study of the sensitivity of O₃ depletion predictions to variations in 5 parameters and 2 reaction rates has been completed, totaling 448 model runs to steady state. The varied parameters were the latitude, altitude, and magnitude of the aircraft emissions, and the background chlorine and aerosol levels. The reactions examined were $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ and $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$. This study differs from Johnston *et al.* (1989) by relying on 2-D model results and including sulfate heterogeneous reactions.

The results support previous conclusions concerning the response of O₃ to HSCTs. The location of the aircraft emissions is the most important determinant of model response. Maximum depletions occur for high altitude, low latitude emissions. Small increases in global total O₃ occur for low altitude, high latitude emissions. Decreases in background chlorine and aerosol levels increase the sensitivity of O₃ to the HSCT emissions, but do not qualitatively change the model response to variations in the location and magnitude of the emissions. Changes in the rates of the two reactions listed above substantially alter the model base simulation, but produce relatively small changes in model sensitivity to HSCT emissions.

Publications

Considine, D. B., C. H. Jackman, and A. R. Douglass, Sensitivity of 2D model predictions of ozone response to stratospheric aircraft, submitted to *J. Geophys. Res.*, April 1994.

Two-Dimensional and Three-Dimensional Model Studies of Stratospheric Aircraft Emissions

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Research Objectives

The goals of this research are: to utilize the 2-D model to calculate the impact of stratospheric aircraft on the ozone layer (assessment calculations); to compare 2-D species values with measurements as tests of the photochemical schemes; to use the 3-D model to evaluate the importance of the buildup of exhaust in flight corridors (the corridor effect); to use the 3-D model to evaluate the importance of middle latitude synoptic scale events to stratosphere/troposphere exchange (STE); to quantify an annual STE budget for HSCT tracers; to use the results from 3-D calculations to evaluate and improve the transport representation in the 2-D model, thereby reducing the uncertainty in the assessment calculations.

Summary of Progress and Results

Results reported in 1993 for 3-D simulations of aircraft exhaust emitted in three corridors showed the possibility of substantial buildup in corridors for specific conditions. However, the distribution for a superposition of several corridors was much more zonally symmetric than the distribution for a single corridor. Therefore the calculations were repeated for the 1979 and 1989 northern hemisphere winters using the distributions of emissions developed for this program. The tracer distributions are fairly symmetric at middle latitudes. As shown previously, almost no tracer is transported into the high latitudes until the final warming due to the stability of the polar vortex.

Significant effort has been placed on understanding the modeled exchange between the stratosphere and troposphere. There are two aspects to the exchange. A long term average can be calculated from the wind fields or can be approximated from the residual circulation. In model calculations, exchange takes place predominantly at middle latitudes, and is strongly associated with synoptic scales. It is not clear that the annual average of the latter processes is

equal to the average calculated from the wind fields or the residual circulation. The 3-D tracer association with synoptic scales is under further investigation, to determine if the model exchange is similar to that calculated with higher resolution mesoscale models. Model tracer behavior is being compared with aircraft and satellite observations. It is planned to compare the lifetime for a tracer for a long term simulation with the lifetime estimated from the wind fields or the residual circulation.

All scenarios requested by the program have been completed using the 2-D model. There have been no major modifications to the 2-D model during the last year. This model has been used to develop a parameterization for the effects of nitric acid trihydrate clouds that can be used for assessment of the impact of HSCT aircraft. The model is also being used for sensitivity studies under a separate investigation (PI, David Considine).

Publications

Cerniglia, M. C., R. B. Rood, and A. R. Douglass, A 3D simulation on the influence of a cut-off low on the distribution of northern hemispheric processed air in late January, 1992, submitted to *J. Geophys. Res.*, 1994.

Considine, D. B., A. R. Douglass, and C. H. Jackman, The effects of a parameterization of nitric acid trihydrate cloud formation on 2D model predictions of stratospheric ozone depletion due to stratospheric aircraft, submitted to *J. Geophys. Res.*, 1994.

Douglass, A. R., R. B. Rood, C. J. Weaver, M. C. Cerniglia, and K. F. Brueske, Implications of 3D tracer studies for 2D assessments of the impact of supersonic aircraft on stratospheric ozone, *J. Geophys. Res.*, 98, 8949-8963, 1993.

Weaver, C. J., A. R. Douglass, and R. B. Rood, Thermodynamic balance of three-dimensional stratospheric winds derived from a data assimilation procedure, *J. Atmos. Sci.*, 17, 2987-2993, 1993.

Weaver, C. J., A. R. Douglass, and R. B. Rood, Tracer transport for realistic aircraft emission scenarios calculated using a three-dimensional model, submitted to *J. Geophys. Res.*, 1994.

Inertia-Gravity Waves in the Stratosphere: Excitation, Propagation, and Constituent Transport

Investigators

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Research Objectives

This study seeks to understand better the excitation of internal inertia-gravity waves (IGW) in the troposphere, their subsequent propagation and breakdown in the lower stratosphere, generation of secondary instabilities, and resulting vertical transport of trace constituents. Such transport is essential for the removal of exhaust pollutants produced by future high-speed aircraft in order to lessen the severity of ozone depletion. We focus specifically on the role of midlatitude synoptic-scale weather systems (baroclinic instability and frontogenesis) in excitation of IGW, refraction into regions of preferred wavebreaking, and the efficiency of *in situ* mixing by convective and dynamical instabilities in breaking IGW.

Summary of Progress and Results

IGW generation by geostrophic adjustment of the tropospheric jetstream is investigated using a high-resolution, large-scale, primitive equation model simulation of tropospheric cyclogenesis. The model's horizontal resolution is approximately 100 km, (T126 spectrally), and vertical resolution 700 m. We find IGW are generated by dynamical imbalances in the exit region of tropospheric jetstreams where parcel acceleration is large. These unbalanced regions may be diagnosed as where the Lagrangian Rossby number exceeds approximately 0.4 while windspeeds are not small. Such IGW generated near the tropopause radiate energy upwards and undergo horizontal refraction towards the jet axis in accordance with linear theory. The IGW have horizontal wavelengths of about 1000 km, vertical wavelengths of up to 4 or 5 km and intrinsic frequencies of up to about three times the Coriolis parameter. These wave properties are in agreement with limited radar observations of lower stratospheric IGW in the vicinity of the tropospheric jetstreams.

IGW can cause significant transport in the lower stratosphere. Such transport can be viewed as an isentropic, quasi-horizontal component associated with the wave's transverse velocity, and a cross-isentropic, vertical mixing component where the waves breakdown via Kelvin-Helmholtz instability. Our large-scale simulations show isentropic transport by IGW in the lower stratosphere resulting in significant quasi-horizontal, cross-jet, parcel dispersion as the IGW approach their critical level above the tropospheric jetstream. Work in progress with a small scale, gravity wave model addresses the cross-isentropic transport associated with upward radiating IGW as they saturate and break by explicitly resolving the secondary instabilities.

Applying the Lagrangian Rossby number diagnostic to global wind data at the level of the jetstream maximum (approx. 250 mb) yields an estimate of the frequency of IGW generation events. The intensity of the resulting IGW radiation depends on the jet windspeed, however, scaling as approximately the square of the core windspeed. Combining the resulting estimate of upward IGW radiation into the lower stratosphere with the cross-isentropic mixing predicted by the small-scale gravity wave model will provide a measure of the vertical diffusivity due to IGW

absorption in the lower stratosphere, a crucial element in modeling the chemical consequences of the proposed high speed civil transport fleet.

Publications

Generation of inertia-gravity waves in simulated mid-latitude baroclinic lifecycles; submitted to *J. Atmos. Sci.*

Airborne Chromatograph for Atmospheric Trace Species (ACATS): Halocarbon, Nitrous Oxide, and Methane Measurements During SPADE and ASHOE

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Research Objectives

The major objectives of this work are to quantify the chlorine budget of the atmosphere and to determine stratospheric lifetimes of ozone-depleting and greenhouse gases. Recent efforts have focused on additional tracer measurements and the comparison of our measurements of methane (CH_4) and nitrous oxide (N_2O) to those of other instruments on the NASA ER-2 aircraft in support of the NASA AESA/HSRP program.

Summary of Progress and Results

The Airborne Chromatograph for Atmospheric Trace Species (ACATS), was developed originally as a one channel gas chromatograph (GC) capable of measuring chlorofluorocarbon (CFC)-11 (CCl_3F) and CFC-113 ($\text{CCl}_2\text{F}-\text{CClF}_2$) once every 120 seconds aboard the NASA ER-2 aircraft during the Airborne Arctic Stratospheric Expedition II (AASE II). In addition to measuring CFC-11 and CFC-113 every 180 seconds, a second GC channel was added for methane (CH_4) measurements during the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) held in April and May 1993. For the Airborne Southern Hemisphere Ozone Experiment (ASHOE) and the Measurements for Assessing the Effects of Stratospheric Aircraft (MAESA) program, a new instrument, ACATS-IV, was developed and operated on the ER-2 aircraft in 1994. This instrument is a gas chromatograph (GC) comprising four separate channels providing *in situ* measurements of chlorofluorocarbons (CFCs), other organic chlorine species, and long-lived tracers in the lower stratosphere and upper troposphere. Measurements of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 ($\text{CCl}_2\text{F}-\text{CClF}_2$), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), nitrous oxide (N_2O), and methane (CH_4) are made in ambient air every 180 seconds.

Figure 1 shows a flight profile of ambient CFC-11 and CH_4 for May 7, 1993 during SPADE. The inset plot shows that mixing ratios of CH_4 are linearly correlated with those of CFC-11. This flight is of particular interest, because the ER-2 aircraft, operated at mid-latitudes, encountered a polar air mass in which the relation of CFC-11 with other long-lived tracers was different than observed in AASE II held from August 1991 through March 1992.

Correlation plots of tracers against a common species, such as those in Figure 2 from the April 8, 1994 flight during ASHOE, can be used to estimate the relative lifetimes of the tracers in the stratosphere using a method similar to those described in Plumb and Ko (1992). Given the observed growth rates, and the prescribed lifetime of 55 years for CFC-11 (Elkins *et al.*, 1993),

we calculated the stratospheric lifetimes for N_2O , CFC-12, CFC-113, CH_3CCl_3 , CCl_4 , and CH_4 as 112 ± 23 (1 s.d.), 103 ± 24 , 127 ± 37 , 56 ± 13 , 47 ± 10 , and 126 ± 26 years, respectively. The sum over the measured organic chlorine species in Figure 2 represents about 80 percent of the total available organic chlorine (CCl_y). Using measurements of CH_4 and N_2O in combination with model correlations of tracers with similar lifetimes, the missing organic chlorine species CH_3Cl and the hydrochlorofluorocarbons (in particular, HCFC -22) can be estimated for each sample and, thereby used to increase the sum to ~97 percent of CCl_y . Available inorganic chlorine (Cl_y) in each sample is then estimated by subtracting CCl_y from the total tropospheric organic chlorine at the time of entry into the stratosphere. Estimates of available inorganic chlorine are crucial to understanding observations of reactive chlorine monoxide (ClO) and hydrochloric acid (HCl) and their role in ozone depletion in the stratosphere. If one understands the contribution of anthropogenic chlorine emissions to the depletion of ozone, an important "greenhouse gas," then it is possible to identify more precisely the effects of aviation on climate change and stratospheric ozone.

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- Plumb, R. A., and M. K. W. Ko, Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res.*, 97, 10145-10156, 1992.

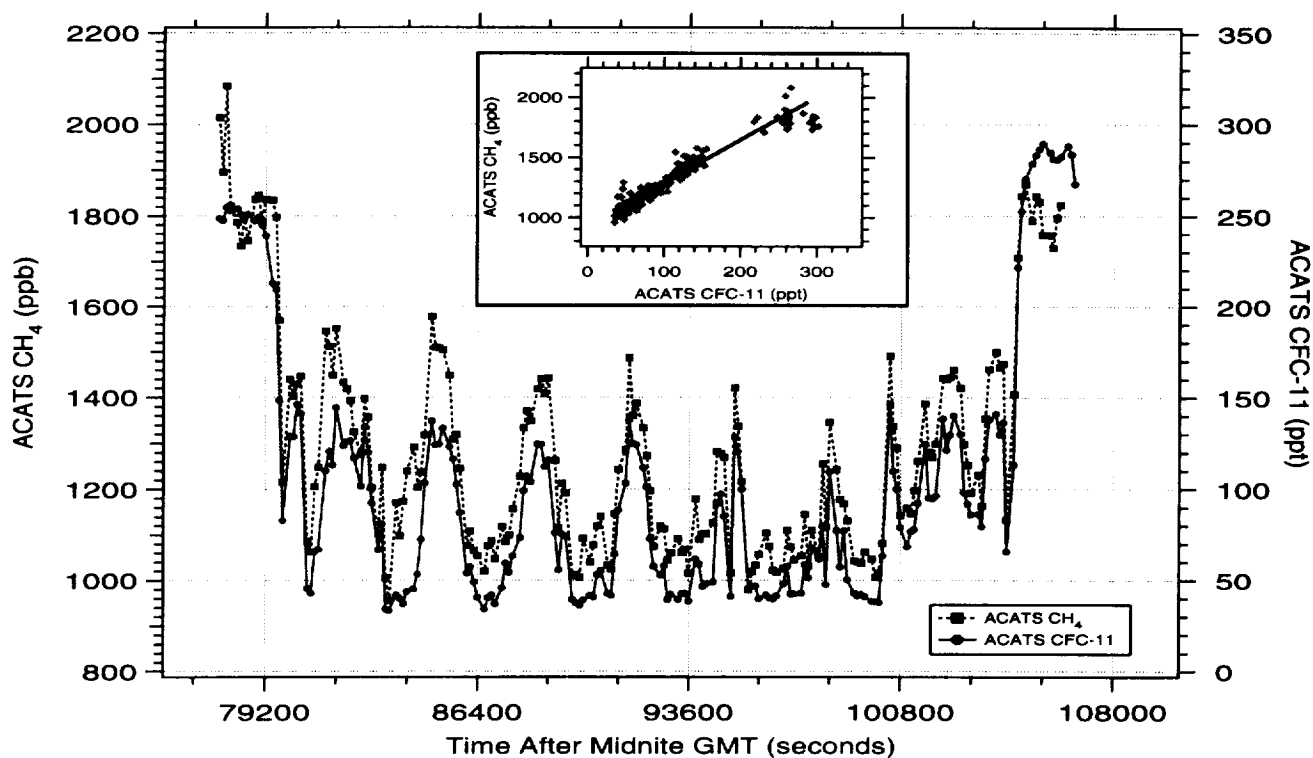


Figure 1. ACATS CH_4 (left) and CFC-11 (right) mixing ratios as a function of time on the flight of the ER-2 aircraft on May 7, 1993 during SPADE. The inset plot shows the strong correlation between the two species for this flight.

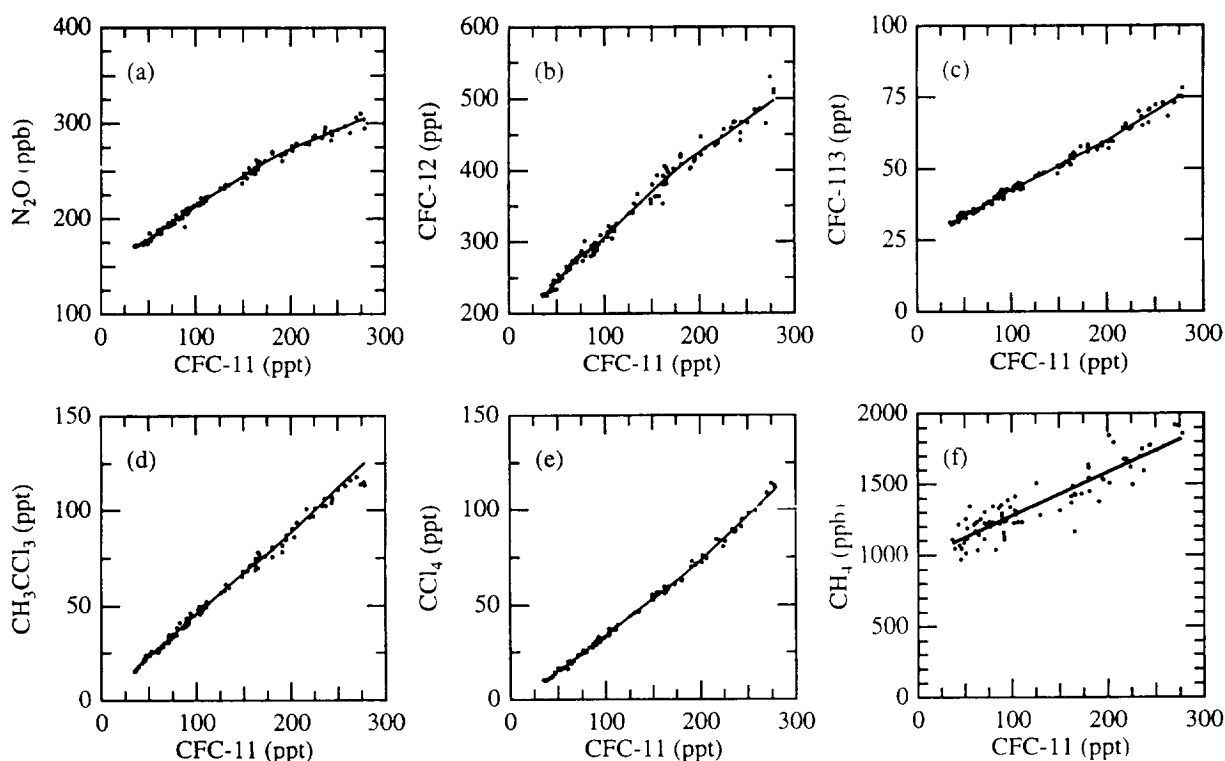


Figure 2. Correlation plots for (a) N_2O , (b) CFC-12, (c) CFC-113, (d) CH_3CCl_3 , (e) CCl_4 , (f) CH_4 versus CFC-11 for the flight of the ER-2 aircraft on April 8, 1994 during ASHOE. All species were measured with the new ACATS-IV instrument.

Publications

Proffitt, M. H., K. Aikin, J. J. Margitan, M. Loewenstein, J. R. Podolske, A. Weaver, K. R. Chan, L. M. Avallone, H. Fast, and J. W. Elkins, Ozone loss inside the northern polar vortex during the 1991-92 winter, *Science*, **261**, 1150-1154, 1993.

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Woodbridge, E. L., J. W. Elkins, D. W. Fahey, S. Solomon, T. J. Baring, T. M. Gilpin, L. E. Heidt, W. H. Pollock, S. Schauffler, E. Atlas, M. Loewenstein, J. R. Podolske, C. R. Webster, R. D. May, R. J. Salawitch, S. C. Wofsy, and S. A. Montzka, Estimates of total organic and inorganic chlorine in the lower stratosphere from *in situ* measurements, submitted to *J. Geophys. Res.*, 1994.

A Dual Channel Chemiluminescence Detector for the Measurements of NO and NO_y Onboard the NASA ER-2 Aircraft

Investigators

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Research Objectives

The research objectives are to design and construct instrumentation for the NASA ER-2 high-altitude aircraft to measure reactive nitrogen species, to participate in field programs that seek measurements of a wide variety of trace species in the lower stratosphere, and to interpret the resulting data in a manner that advances our understanding of the photo-chemistry and dynamics of the lower stratosphere.

Summary of Progress and Results

The NASA Stratospheric Photochemistry, Aerosol and Dynamics Experiment (SPADE) ended in May 1993 with data for NO, NO₂, and NO_y obtained in the lower stratosphere. Submission of final data was completed in summer 1994. Interpretation of these data along with other species and parameters measured onboard the ER-2 has occurred in the following areas:

- Measurements of NO₂ were acquired with a new photolytic converter/chemiluminescence system developed for SPADE. Flights during which the terminator was crossed at both sunrise and sunset provided the best data sets. In darkness, NO is removed in reaction with O₃ to form NO₂. The resulting change in the NO/NO₂ ratio across the terminator will be used to evaluate radiation field calculations at high solar zenith angles.
- The appearance of NO at sunrise follows the photolysis of NO₂ at wavelengths near 400 nm. The comparison of the appearance of NO with that of OH suggests a secondary source for OH at similar wavelengths. Photochemical models with full diurnal chemistry are being used to simulate this additional source.
- The partitioning of HO₂ to OH in the lower stratosphere can be modeled using reactions with NO, O₃, CO, and halogen species. Reactions involving NO and O₃ usually predominate. Excellent agreement is found between the model partitioning and the observed HO₂/OH ratio. The systematic agreement suggests reduced uncertainty limits for the rate constant expressions used in the model.

- The ER-2 instruments have been used to observe ER-2 engine exhaust in the lower stratosphere. Measurements include total reactive nitrogen, NO_y , the component species NO and NO_2 , CO_2 , H_2O , condensation nuclei, and meteorological parameters. The simultaneous measurements of reactive nitrogen and CO_2 are converted to an emission index (EI) for NO_x of $4 \text{ gm (kg fuel)}^{-1}$ which is in good agreement with values scaled from limited ground-based tests of the ER-2 engine. Non- NO_x species comprise less than about 20 percent of emitted reactive nitrogen, consistent with model evaluations.

In other efforts, measurements of organic chlorine species taken during the Airborne Arctic Stratospheric Expedition II (AASE II) were used to estimate the burden of organic and inorganic chlorine in air parcels in the lower stratosphere. Data sets from the Whole Air Sampling instrument and a gas chromatograph operating *in situ* were used. Values of N_2O , a long-lived tracer, provided an index to the age of stratospheric air samples necessary to estimate the organic chlorine burden in an air parcel upon entry to the stratosphere. Consistent results are found for the decrease in organic chlorine with decreasing N_2O over a wide range of N_2O . Since total chlorine is conserved in an air parcel, inorganic chlorine can be equated to the change in organic chlorine.

Finally, the Reactive Nitrogen instrument was prepared for participation in the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA). Calibration procedures were completed and ground support facilities were improved. Initial test flights at Ames Research Center were successfully completed in February 1994.

Journal Publications

Lead authors:

Fahey, D. W., E. R. Keim, E. L. Woodbridge, R. S. Gao, K. A. Boering, B. C. Daube, S. C. Wofsy, R. P. Lohmann, E. J. Hints, A. E. Dessler, C. R. Webster, R. D. May, C. A. Brock, J. C. Wilson, P. O. Wennberg, R. C. Cohen, R. C. Miake-Lye, R. C. Brown, J. M. Rodriguez, M. Loewenstein, M. H. Proffitt, R. M. Stimpfle, S. W. Bowen, and K. R. Chan, *In situ* observations in aircraft exhaust plumes in the lower stratosphere at mid-latitudes, submitted to *J. Geophys. Res.*, 1994.

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Contributing authors:

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Homogeneous and Heterogeneous Chemistry of Odd Nitrogen Species Related to Stratospheric Aircraft

Investigators

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Research Objectives

Our aim is to improve the laboratory data base for several important odd nitrogen reservoir species, namely peroxyntiric acid (PNA) and peroxyacetyl nitrate (PAN). Our specific focus is on processes that may impact the partitioning between nitrogen oxides. Consequently we are investigating the product yields of NO_2 and NO_3 from photolytic decomposition of PAN and PNA and possible heterogeneous conversions of PAN and PNA to HNO_3 .

Summary of Progress and Results

1) We examined the interaction of PNA with H_2O -ice using a fast flow reactor coupled to a mass spectrometer. The surface studies revealed that PNA uptake on ice occurs rapidly and irreversibly. An uptake coefficient of 0.15 ± 0.10 was measured for the process. The fate of the PNA on the ice was investigated by performing programmed temperature desorptions of the surface adsorbates. No reaction products other than PNA were found during these trials. The observed desorption behavior of the PNA suggests that it exists in a hydrated form on or in the ice. These results indicate that PNA, like HNO_3 , may be removed from the springtime Antarctic stratosphere by subsidence of polar stratospheric clouds.

2) We measured NO_2 and NO_3 product yields from photolysis of PAN at 248 nm. The laser induced fluorescence detection method was successfully applied to both NO_2 and NO_3 . A NO_2 quantum yield of 0.83 ± 0.14 was determined from the fluorescence data after we completed a detailed consideration of the internal energy relaxation of the nascent NO_2 . No apparent production of NO_3 was observed. We have placed a preliminary upper limit of 0.2 on the yield of NO_3 . This upper limit is consistent with the NO_2 yield data.

Publications

Mazely, T. L., R. R. Friedl, and S. P. Sander, Measurement of the V-T energy transfer rates of highly excited $^2\text{A}_1 \text{NO}_2$, *J. Chem. Phys.*, **100**, 8040-8046, 1994.

Particulate Emissions Characterization for HSCT Related Tests on Flame Tubes, Annular Sector Combustor Rigs and Jet Engines

Investigators

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Research Objectives

The research objective is the experimental characterization of jet engine emissions with regard to particulate production, interaction with other gaseous emissions, and their evolution in the atmosphere. Major progress was made on tasks 1 (MASS automation upgrade), 2 (MASS back-up system construction and calibration), 9 (Data Interpretation, Inter-Device, and Inter-Study Correlations and Comparisons), and 11 (Complementary Laboratory Measurements) as described in the statement of work section 2.0 of our grant proposal. Ground work including a site visit has been undertaken on task 5. Work performed under this grant was also presented at the NASA workshop on emissions characterization, held at Aerodyne Inc., in November 1993.

Summary of Progress and Results

Laboratory experiments completed to date include: system leaktests, development of deliquescence experiment procedure, saturator relative humidity level tests, comparison of total CN count with integrated size distribution, aerosol loss tests for different possible sample line materials, CN counter efficiency, sample line time delay measurements, sample holding tank depletion coefficient measurements, and aerosol loss in sample preparation devices.

Project results have been presented at several conferences:

Hagen, D. E., P. D. Whitefield, M. B. Trueblood, and H. V. Lilenfeld, Particulates and aerosols characterized in real time from harsh environments using the UMR mobile aerosol sampling system (MASS), AIAA Joint Propulsion conference and exhibit, Monterey, CA, June 1993.

Hagen, D. E., P. D. Whitefield, and M. B. Trueblood, Particulate characterization in the near field of commercial transport aircraft exhaust plumes using the UMR-MASS, Impact of emissions from aircraft and spacecraft upon the atmosphere Symposium, Cologne, Germany, April 1994.

Whitefield, P. D., D. E. Hagen, M. B. Trueblood, and H. V. Lilenfeld, Real-time characterization of combustion particulates and aerosols from jet engine emissions in flight and during ground tests using a Mobile Aerosol Sampling System (MASS), 18th General Assembly of the European Geophysical Society session on Aviation and space flight: Impact on the atmosphere, May 1993.

Whitefield, P. D., D. E. Hagen, W. M. Barnett, and H. V. Lilenfeld, *Particulate emissions characterization and reactivity*, NASA High Speed Research Program Annual meeting, Virginia Beach, VA, June 1993.

Whitefield, P. D., D. E. Hagen, and M. B. Trueblood, Exhaust particulate characteristics of a high performance GE-404 jet engine, 24th Annual Meeting of the Fine Particle Society, Chicago, IL, August 1993.

Publications

None

Problem of the Heterogeneous Hydrolysis of Acid Anhydrides on Stratospheric Sulfate Aerosols

Investigator

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Research Objectives

A main objective of the theoretical component of the SPADE program was to develop a numerical model to study the interaction between stratospheric gases and stratospheric particulates. This model, known by the acronym GUMBO, was intended for use in interpreting the ER-2 measurements made under the auspices of the SPADE program. Therefore, back trajectories of the air parcels sampled by the ER-2 were evaluated. Photochemical reactions from the models of Salawitch and Prather were used to evaluate the concentrations of gaseous species. Heterogeneous chemistry was used to evaluate the effect of particulates on gas phase concentrations. An important parameter to be determined was the surface area of the sulfate particles involved in the heterogeneous chemical reactions. The particular objective of this research project was to develop an algorithm to determine the surface area of the particles along the back trajectory. This algorithm was to be incorporated into the GUMBO model.

Summary of Progress and Results

A program was developed to evaluate the size distribution of the sulfate aerosols. This program used the number densities obtained from the FSSP instrument on the ER-2 and fitted them to a zero order logarithmic size distribution. It is known that the aerosol particles in the stratosphere are composed of sulfuric acid and water and are in equilibrium with respect to water. Changes in temperature will affect the vapor pressure of water of the solution droplets and they will respond by either absorbing or evaporating water until equilibrium is reached again. The size distribution is then assumed to change only via this evaporation or condensation of water, a mechanism which is a function of the environmental temperature and the environmental water concentration. Since these quantities are known along the back trajectory, it is possible to evaluate changes in the particle size distribution and, hence, to calculate the total surface area of the particles. The output is the total surface area of the particles as a function of time along the air parcel back trajectory. This program was successfully incorporated into the GUMBO model as a subroutine.

Publications

None

Environmental Impact of High-Flying Aircraft Studied Using Two-Dimensional Models

Investigators

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Research Objectives

Assessment of global-scale changes produced by aircraft exhausts, using a model which permits the effects of most radiative-chemical-dynamical feedbacks and natural variability to be incorporated.

Summary of Progress and Results

Over the past year the model (Kinnersley and Harwood 1993) has been improved in a number of ways, an explicit representation of the three longest planetary waves has been included, and a parametrisation of the effects of the shorter planetary waves developed. The planetary wave model has been shown to reproduce observed waves rather well (Kinnersley 1994). The model also now includes a gravity-wave parametrisation, which produces a realistic semi-annual oscillation in the modelled wind and chemical fields, and a fairly realistic behavior of the stratospheric and mesospheric jets. A parametrisation of Kelvin and Rossby-gravity waves has recently been included, resulting in an equatorial quasi-biennial oscillation which, because of the interaction between modelled waves and zonal-mean state, affects the extra-tropics. The model is thus a useful tool for investigating the nature of the extra-tropical inter-annual variability. It has already been used to investigate the effect on the stratosphere of inter-annually varying wave amplitudes at the tropopause.

A crude parametrisation of polar stratospheric clouds has been included in the chemical scheme, which uses the longitudinal variations in temperature due to the modelled planetary waves to determine over which fraction of a latitude circle the clouds are present. The effects of aerosols are now treated not only for chemistry, but also for solar heating and photodissociation rates. Some improvements have also been made to the advection scheme leading to more realistic chemical and wind fields; the treatment of thermal wind balance of the zonal-mean state again leading to better wind fields; and, the treatment of convective and baroclinic instabilities in the troposphere. The aim of these enhancements is to produce as good a chemical-dynamical model of the atmosphere as possible so that assessments of the impact of atmospheric pollutants, such as aircraft emissions, will have the highest validity. Great emphasis is placed on comparing modelled trace gases with the latest observations in an attempt to diagnose model deficiencies.

Publications

Kinnersley, J. S., and R. S. Harwood, An isentropic two-dimensional model with an interactive parametrisation of dynamical and chemical planetary-wave fluxes, *Quart. J. R. Met. Soc.*, **119**, 1167-1193, 1993.

Kinnersley, J. S., A realistic three-component planetary wave model, with a wave-breaking parametrisation, submitted to *Quart. J. Roy. Met. Soc.*, 1994.

Project and Data Management Support for HSRP Field Missions

Investigators

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Research Objectives

To provide project management for HSRP aircraft field campaigns, including data management and computer networking support. Project management covers a range of activities, including assistance in experiment definition, scheduling, field facility preparation, dissemination of project information, overseeing aircraft payload integration, and projecting and tracking deployment budgets. Data management entails the definition of data exchange standards and implementation of the exchange process in the field. It also includes the dissemination of the field experiment datasets after the mission. Networking support provides the basis for the data exchange in the field; it also provides the communication link for acquiring critical datasets required during the field missions and for communication to home labs.

Summary of Progress and Results

The SPADE mission was completed in May 1993 and was extremely successful, producing a rich new dataset with many new measurements. The SPADE dataset was published on CDROM and distributed to the SPADE team.

The preparations for the 1994 Airborne Southern Hemisphere Ozone Experiment (ASHOE) and Measurements for the Assessing the Effects of Stratospheric Aircraft (MAESA) were completed in March 1994. This included set-up of temporary lab facilities at NASA Ames, Barber's Point, Hawaii, and Christchurch, New Zealand. Internet links and a local area network (LAN) were established for all three sites.

The first deployment phase of the experiment was completed in mid-April and was a major success. All intended flights were accomplished including the transit flights from NASA Ames, tropical flights locally from Barber's Point, and flights to the north and south of Christchurch. Twelve science flights were made in all during the first phase.

Publications

SPADE Mission Dataset CDROM, P. G. Hathaway, S. E. Gaines, S. Hipskind, editors, HSRP-001, Edition 1, January 1994.

Dynamical and Chemical Studies of Aircraft Emissions Using Satellite Data and a 2-D Model

Investigator

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Research Objectives

We proposed to assess the effects of high speed aircraft by using satellite data, aircraft mission data, and a 2-D model, focussing on two specific areas: heterogeneous effects of sulfate aerosols and gravity waves and vertical tracer transport.

Summary of Progress and Results

This grant has supported a graduate research assistant, including Megan McKay, (M.S., May 1993) and, more recently, Lynn Harvey. The primary result of our work is the aerosol climatology, which we have archived at the Langley Research Center DAAC for use by the community. We have carried out model investigations with this aerosol climatology under various aircraft scenarios. A secondary focus has been to improve the latitude, altitude and seasonal dependence of vertical mixing coefficients near the tropopause. This was done through consideration of the observed seasonal shift in tropopause location and turbulent mixing implicated by ST radar observations, while maintaining fidelity with zonal mean distributions of several tracers observed by satellite.

Our global climatology of stratospheric aerosol was created by combining nearly a decade of SAGE I and II and SAM II data. This work has provided a representative distribution of the aerosol layer for use in radiative and chemical modeling. We find that the aerosol layer is distinctly volcanic in nature and suggest that the decadal average is a more useful estimate of future aerosol loading than a "background" loading, which is never clearly achieved during the data record.

This climatology also lends insight into the general circulation of the stratosphere. A tropical reservoir region is diagnosed, with an "upper" and a "lower" transport regime. In the tropics above 22 km (upper regime), enhanced lofting occurs in the summer, with suppressed lofting or eddy dilution in the winter. In the extratropics within two scale heights of the tropopause (lower regime), poleward and downward transport is most robust during winter, especially in the northern hemisphere. The transport patterns persist into the subsequent equinoctial season. Ascent associated with QBO easterly shear favors detrainment in the upper regime, while relative descent and poleward spreading during QBO westerly shear favors detrainment in the lower regime. Extinction ratio differences between the winter-spring and summer-fall hemispheres, and differences between the two phases of the QBO, are typically 20-50 percent.

Publications

Hitchman, M. H., M. A. McKay, and C. R. Trepte, A climatology of stratospheric aerosol, *J. Geophys. Res.*, 99, 20689, 1994.

The Impact of NO_x Emissions on Ozone from a Future Fleet of High Flying Aircraft

Investigators

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Research Objectives

The objectives have been to study the impact on ozone of NO_x emitted from a future fleet of supersonic aircraft flying in the lower stratosphere, and to study the sensitivity of the ozone perturbations to heterogeneous chemistry in the lower stratosphere and to the stratospheric chlorine loading. Heterogeneous chemistry primarily affects speciation of chlorine compounds and chlorine loading through the strong linkage of the NO_x chemistry in the lower stratosphere with the chlorine chemistry through the reaction of ClO with NO₂. Therefore, a main task is to study how the heterogeneously induced ozone reduction by chlorine and bromine reactions in the lower stratosphere is affected by enhanced NO_x emission.

Summary of Progress and Results

The parameterization of the heterogeneous chemistry in the model is updated to include the recently updated values for the reactions of nitrogen and chlorine compounds on particles in the stratosphere. Heterogeneous reactions of N₂O₅, ClONO₂, HCl, and OHCl on background particles in some runs also on PSCs, are included in the calculations. Time-dependent calculations until 2015 are performed for a base case where NO_x emissions from supersonic aircraft are not included. Several model calculations with NO_x emissions from supersonic aircraft are also done. In these calculations the height of the emission is varied corresponding to a speed of 1.6 to 2.4 Mach, and three different emission indices (5, 15, and 45 [NO₂]/kg fuel) are used. Calculations have also been performed for two different chlorine levels.

The 2-D model calculations with the adopted scenarios resulted in a small increase in ozone in the case of Mach 1.6. When watervapor emitted from the aircraft is included in model, an even smaller increase in ozone is seen. In the case with Mach 2.4 corresponding to a flight-height of about 21 km, a little decrease is seen in ozone. In this case a higher decrease is seen if watervapor is included. Comparing the two chlorine loading cases, one with 2.0 ppbv Cl_y, and one with 3.7 ppbv, a larger decrease in ozone is seen in the lower case. When NO_x is emitted at about 21 km (Mach 2.4) transportations to lower altitudes are seen, which is not seen at Mach 1.6.

Publications

Isaksen, I. S. A., O. P. Berge, and B. Rognerud, The impact of NO_x emissions on ozone from a future fleet of high flying aircraft, to be submitted.

NO/NO_y, O₃ and H₂O Instruments, and Meteorological Analysis

Investigator

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Research Objectives

Water measurements and intercomparisons.

Summary of Progress and Results

The lyman alpha instrument was modified for SPADE II in order to reduce the weight and the forebody moment. This instrument was flown during SPADE II and the mini mission in October. The instrument failed to calibrate during the mini mission. The reduced thermal control in the new package could not maintain the instrument temperature without the other payloads in the Q bay.

The instrument was compared in the lab to NOAA CMDL's frost point instrument before and after SPADE II. The agreement was better than the calculated uncertainties. One of three balloon measurements during SPADE II agreed with the aircraft measurement. The other two were off by the historical difference. The atmosphere was highly variable and the overlap was not good which makes a comparison difficult. Harvard also flew a lyman alpha hygrometer as part of the OH instrument. The Harvard measurements were higher than both NOAA measurements. A post mission review of both lyman alpha instruments could find no operational or calibration errors. One difference is in the calibration technique. The NOAA calibration is based on the lyman alpha absorption cross section of water vapor measured with reference to the vapor pressure over ice. The Harvard calibration is based on air saturated with respect to water and then mixed with dry air. Harvard has offered to do a lab intercomparison with NOAA using their technique.

Publications

None

Impact of Engine Emissions of a Proposed High-Speed Stratospheric Aircraft Fleet on the State of the Atmosphere

Investigators

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Research Objectives

The AER 2-D chemistry-transport model is used to investigate the sensitivity of ozone to emissions from HSCT aircraft, including nitrogen oxides, water vapor, carbon monoxide, hydrocarbons, and sulfur dioxide. Our collaboration with Dr. Glenn Yue of NASA Langley has resulted in implementation of a sulfate model that allows us to predict changes in aerosol surface area due to aircraft emission. Our work will also explore the limitation of 2-D models in parameterizing stratospheric/tropospheric exchange, and the limitation in accounting for the initial redistribution of material emitted by aircraft before they become zonally-mixed.

Summary of Progress and Results

The aerosol code which was supplied to us by Dr. Glenn Yue of NASA Langley has been incorporated into our gas phase sulfate chemical transport model. We have used our aerosol model to simulate the effect of aircraft emissions on the aerosol. The model results showed that the injected SO₂ and H₂O increase the size of existing particles rather than forming new particles, which results in faster sedimentation. Thus the overall increase in stratospheric aerosols due to HSCT emissions is less than would be predicted if the aerosol size distribution were assumed constant. Our previous study also showed that the e-folding time for aerosol removal from the stratosphere was found to be 30-50 percent shorter than the observed time constant for volcanic aerosol. Work is continuing to validate our model results.

AER is working with GSFC in a photochemistry intercomparison exercise designed to ascertain some of the reasons for the different model predicted ozone response to HSCT emissions between the two models.

Publications

- Plumb, R. A., M. K. W. Ko, and R.-L. Shia, Representation of localized NO_x emissions in a two-dimensional model of the stratospheric ozone, submitted to *J. Geophys. Res.*
- Shia, R.-L., M. K. W. Ko, M. Zou, and V. R. Kotamarthi, Cross tropopause transport of excess ¹⁴C in a two-dimensional model, *J. Geophys. Res.*, 98, 18599-18606, 1993.
- Weisenstein, D. K., M. K. W. Ko, J. M. Rodriguez, and N. D. Sze, Effects on stratospheric ozone from high-speed civil transport: Sensitivity to stratospheric aerosol loading, *J. Geophys. Res.*, 98, 23113-23140, 1993.

Design and Development of an Unmanned Research Aircraft in Support of the Small High Altitude Science Aircraft (SHASA) Project

Investigator

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Research Objectives

Develop and field two Perseus A science aircraft capable of carrying a 50 kg payload to altitudes in excess of 25 km.

Summary of Progress and Results

In the interval since the last program report the first two Perseus A aircraft have been completed and delivered to Dryden Flight Research Center for the start of flight test. The first flight occurred on December 21, 1993, accumulating a total of 57 minutes of flight time. Through March 14, an additional six flights have been completed for a total of approximately 13 hours of flight time. The initial seven flights were dedicated to procedures and systems testing and autopilot validation. To date, all flights have been successful with the following procedural and functional milestones achieved:

Towed launch - a series of seven towed launches have validated the auto-tow concept using a constant tension reel assembly. All tows have been uneventful with peak altitudes of 900-1200 feet established before aircraft release.

Propeller engagement sequence - more than 15 airborne engagements have been conducted without incident. The engagement sequence consists of unlocking the propeller from its horizontal launch position, windmilling to match engine speed, and automatically triggering driveline clutch engagement. Each flight has concluded with propeller disengagement, feathering, and lock in horizontal position. Use of variable pitch on the locked propeller has been validated as the primary means of glide path control during descent to landing.

Aero performance checks - satisfactory low altitude aircraft aerodynamic performance has been demonstrated with measured L/D within 10 percent of predicted values. Aircraft dynamics during tow and in flight closely match those predicted by simulation.

Autopilot validation - an extensive series of autopilot tests has validated each of the six levels of autopilot function that are contained within the core Ithaca flight control software. Beginning with the first flight, bank hold, airspeed hold, and side slip hold autopilots were activated upon commencing the tow. Later flights validated the function of the more complex autopilot levels including lost link, heading hold, and full automatic waypoint navigation. The aircraft demonstrated autonomous flight with all radio links intentionally severed on its third flight. Completion of this phase of testing clears the aircraft for beyond visual range operations at higher altitudes.

The balance of the flight test is dedicated to achieving full altitude capability by the end of April 1994.

Publications

None

Laboratory Studies of Heterogeneous Processes Important in Stratospheric Aircraft Emissions

Investigators

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Research Objectives

This task focuses on the investigation of heterogeneous processes which are potentially important in assessing the environmental effects of high-altitude aircraft emissions. The work aims to concentrate on the effects of water ice (Type II PSCs), nitric acid trihydrate (Type I PSCs), sulfuric acid aerosols, and soot on atmospheric species important in the HO_x , NO_x , and ClO_x cycles which include: N_2O_5 , HNO_3 , HCl , HOCl , and ClONO_2 . Flow-tube reactors interfaced with quadrupole mass spectrometers (using both electron-impact ionization and chemical ionization) are used to measure reaction or sticking probabilities on these aerosol surfaces. Several analytical techniques which include mass spectrometry, infrared spectrometry, environmental and conventional scanning electron microscopies, x-ray elemental analysis, and low-temperature adsorption (BET analysis) are used to identify products and to characterize the condensed phase.

Summary of Progress and Results

Laboratory Activities under this task during 1993 and 1994 concern the heterogeneous chemistry on the surface of polar stratospheric clouds. Accomplishments include:

Morphology of Nitric Acid and Water Ice Films: Ice films have been used to simulate stratospheric cloud surfaces in order to obtain laboratory data on solubilities and heterogeneous reaction rates. To obtain intrinsic uptake and surface reaction probabilities which can be applied to atmospheric models, it is necessary to carefully characterize these films. In the present study, environmental scanning electron microscopy is used to study thin films of both water ice and nitric acid ice near the composition of the trihydrate. The ices are formed by vapor deposition onto aluminum or borosilicate-glass substrates cooled to about 200 K. Micrographs are recorded during the deposition process and during subsequent annealing at higher temperatures. The results show that the ice films are composed of loosely consolidated granules, which range from about 1 to 20 μm in size at temperatures between 197 and 235 K. Cubic water ice is sometimes observed at 200 K and converts to the hexagonal form at slightly higher temperatures. The loose packing of the granules confirms the high porosities of these films obtained from separate bulk porosity measurements. Average surface areas calculated from the observed granule sizes range from about 0.2 to 1 $\text{m}^2 \text{g}^{-1}$ and agree with surface areas obtained by gas-adsorption analysis of annealed ice films.

Uptake of HCl in Water Ice and Nitric Acid Ice Films: The uptake of HCl in water ice and nitric acid ice films is investigated in a flow reactor interfaced with a differentially pumped quadrupole mass spectrometer. These studies are performed under experimental conditions that may mimic the polar stratosphere. The HCl uptake in ice films at 188 and 193 K is determined to be in the range of 8.7×10^{13} to 1.8×10^{15} molecules/ cm^2 (if the geometric area of the flow reactor is used in the calculation) when HCl partial pressures of 7×10^{-8} to 6×10^{-6} Torr are used. On the basis

of a model which accounts for the total surface area of the films, the true surface density could be a factor of 25 lower than that calculated by the geometric area. The uptake of HCl in nitric acid ice at 188 K is determined to be in the range of 8.0×10^{13} to 5.3×10^{14} molecules/cm² at a HCl partial pressure of 4.5×10^{-7} Torr.

Reaction Probability Measurements: Heterogeneous reactions of $\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ (1) and $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$ (2) on ice surfaces at a temperature of 188 K are investigated in a flow reactor interfaced with a quadrupole mass spectrometer. Both the decay rates of HOCl and ClONO₂ and the growth rates of Cl₂ are used to obtain reaction probabilities: $\gamma_g(1) = 0.34 \pm 0.20$ and $\gamma_g(2) = 0.27 \pm 0.19$ if we assume that the area of ice surfaces is equal to the geometric area of the flow-tube reactor. By considering the morphology of ice films, we obtain true reaction probabilities: $\gamma_t(1) = 0.13 \pm 0.08$ and $\gamma_t(2) = 0.10 \pm 0.08$ using a previously published model of surface reaction and pore diffusion. In addition, the true reaction probability for the $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$ reaction is measured to be greater than 0.03 on ice surfaces.

Publications

Chu, L. T., M.-T. Leu, and L. F. Keyser, Heterogeneous reactions of $\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ and $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$ on ice surfaces at polar stratospheric conditions, *J. Phys. Chem.*, 97, 12798, 1993.

Chu, L. T., M.-T. Leu, and L. F. Keyser, Uptake of HCl in water ice and nitric acid ice films, *J. Phys. Chem.*, 97, 7779, 1993.

Keyser, L. F., and M.-T. Leu, Morphology of nitric acid and water ice films, *Microscopy Res. and Technique*, 25, 434, 1993.

Keyser, L. F., and M.-T. Leu, Surface areas and porosities of ices used to simulate stratospheric clouds, *J. Colloid and Interface Sci.*, 155, 137, 1993.

Keyser, L. F., M.-T. Leu, and S. B. Moore, Comment on porosities of ice films used to simulate stratospheric cloud surfaces, *J. Phys. Chem.*, 97, 2800, 1993.

Argus: A Dual Channel Tracer Instrument for Stratospheric Measurements of CH₄ and N₂O

Investigator

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Research Objectives

Inert tracers provide an essential “coordinate” in multi-constituent stratospheric chemical and dynamical studies. In probing the stratosphere to altitudes of 25 km and above, the current program for the Perseus A aircraft, N₂O (nitrous oxide) and CH₄ (methane) are measurable tracers which will provide this coordinate. The Argus instrument, which we are currently building, is a dual channel diode laser spectrometer designed to give accurate (3 percent) tracer fields over the Perseus operational envelope at a data rate of one measurement per 10 seconds.

Summary of Progress and Results

During the past year, a prototype of the Argus instrument has been built and tested. All design specifications have been met by this single channel model of Argus employing a 12 meter (total path) Herriott-type off axis resonator used as a sampling cell for the *in situ* measurement.

Based upon experience gained with the lab prototype, final instrument design was completed and fabrication of the flight instrument was begun in the latter half of 1993. Many flight-hardware components are now complete or nearing completion; a finished instrument will be ready for lab and flight testing by mid-1994.

An additional effort of the past year has been the design of the Argus data analysis system. It is based upon an SGI (Unix) workstation running the IDL programming language. Non-linear least squares (Marquardt algorithm) fits of data (2nd harmonic spectra) from the prototype instrument have been carried out for simulated stratospheric conditions. A continuing effort involves streamlining the data analysis protocols for more efficient reduction of the tracer data in the field operational environment.

When completed Argus will be a unique, light-weight, accurate instrument for stratospheric field measurements. Following in the tradition of the highly successful ATLAS instrument Argus will play a key role in the vigorous future of stratospheric research.

Publications

None

The Interaction of Engine Exhaust Plumes and Wing Wake Vortices

Investigators

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Research Objectives

The environmental perturbations caused by the exhaust of a High Speed Civil Transport (HSCT) depend on the deposition altitude and the amount and composition of the emissions. The chemical evolution and the mixing and vortical motion of the exhaust need to be analyzed to track the exhaust and its speciation as the emissions are mixed to atmospheric scales. A numerical model of the dynamical and chemical processes in the aircraft vortex wake is being developed based on the existing UNIWAKE wake code. The vortex wake calculation is initialized with plume mixing and chemistry, using the SPF model, and with the rolled-up wing-tip vortices from a representative HSCT configuration. The subsequent chemical evolution and motion of the exhaust gases in the descending vortex cell are followed in this numerical model. In addition, the resulting flowfield, including both temperature and species concentrations, defines the environment in which aerosol formation and growth may proceed. The species tracked include those that could be heterogeneously reactive on the surfaces of the condensed solid water (ice) particles when condensation occurs, and those capable of participating in the formation active contrail and/or cloud condensation nuclei.

Summary of Progress and Results

The chemistry/condensation model has been extended from the near-field jet regime through the vortex regime to the point of vortex instability. The evolution of SO_x and NO_y plume speciation is followed using a detailed kinetic mechanism for H/O/C/S/N chemistry, with binary homogenous $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ nucleation and gas phase oxidation kinetics coupled to provide more realistic estimates for levels of H_2SO_4 and properties of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ nucleation embryos. The kinetically limited growth of water droplets and ice particles is implemented as an overlay on flowfield streamlines in the jet regime and along the trajectories of tracers in wake-vortex regime. Initial estimates are provided for the effects of coagulation on condensation nuclei. Also, calculations for the NASA ER-2 have been performed to simulate the SPADE wake crossing event. They provide an estimate of NO_y levels that is within a factor of 2-3 of the values measured in the SPADE campaign.

Publications

Brown, R. C. *et al.*, manuscript(s) in preparation.

Fahey, D. W., E. L. Keim, E. L. Woodbridge, R. S. Gao, K. A. Boering, S. C. Wofsy, E. Hints, C. A. Brock, J. C. Wilson, R. P. Lohmann, R. C. Miake-Lye, R. C. Brown, M. Lowenstein, M. H. Proffitt, R. M. Stimpfle, S. W. Bowen, and K. R. Chan, Observations of aircraft exhaust in the lower stratosphere: The emission index of reactive nitrogen oxide species, submitted to *J. Geophys. Res.*, 1994.

Miake-Lye, R. C., R. C. Brown, M. Martinez-Sanchez, and C. E. Kolb, High speed civil transport exhaust mixing and chemistry, presented at the JANNAF Exhaust Plume Technology Subcommittee Meeting, Kirtland AFB, 10 February 1993. CPIA Publication 595, Chemical Propulsion Information Agency, 317-325, 1993.

Miake-Lye, R. C., R. C. Brown, M. Martinez-Sanchez, and C. E. Kolb, Dynamics, mixing, and chemistry of HSCT aircraft exhaust, presented at IMechE Seminar on Aero Fuels, Combustion and the Environment, Birmingham, U.K., 16 September 1993.

Development of Trace Gas Constituent Measurement Techniques for HSCT Engines and Their Components

Investigators

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Research Objectives

The objective of this program is the detailed characterization of engine exhaust trace constituents, motivated by the need to quantify levels of species that are active in homogeneous and heterogeneous chemistry and condensation in the plumes and wakes of high-speed civil transport (HSCT) aircraft. Accurate inputs to both plume/wake models and global atmospheric models require complete and accurate accounts of SO_x and NO_y being injected into the atmosphere. Work is divided into three areas: assessment and prioritization of the required exhaust composition measurements for both existing gas turbine engines and prototype HSCT engine components; an optimal Tunable Diode Laser (TDL) absorption technique to measure high-priority species concentrations; and, instrument development and characterization based on this design carried out at ARI, followed by a measurement program at HSRP-selected combustor development sites. These measurements will verify the sensitivity and detectability of the trace species and will provide emission estimates of these species for use in the AESA atmospheric assessment program.

Summary of Progress and Results

A portable infrared tunable diode laser apparatus has been assembled and tested which is capable of both *in situ* line-of-sight and extractive sampling of combustion gas flows. Infrared diode laser absorption was chosen to be sensitive, quantitative, and applicable to a wide range of molecular species. In the present apparatus, sensitive detection is achieved by rapid frequency scanning and real-time nonlinear least squares fitting and background subtraction. Sensitivity is further increased for extractive sampling by an advanced design multiple pass cell which gives longer path lengths in smaller volumes. Observations of a laboratory flat flame burner, and the results of the first field test at a combustor simulator at the NASA Lewis Research Center, have been completed and are described in the referenced report. These observations and spectroscopic models are used to predict detection sensitivities in exhausts and other combustion systems.

Publications

Miake-Lye, R. C., W. J. Dodds, D. W. Fahey, C. E. Kolb, and S. R. Langhoff, Engine trace constituent measurements recommended for the assessment of the atmospheric effects of stratospheric aircraft, Aerodyne Research, Inc, Report ARI-RR-947, August 1992; also Chapter 5, in *The Atmospheric Effects of Stratospheric Aircraft: A Third Program Report*, M. J. Prather and H. L. Wesoky, editors, NASA Reference Publication 1313, 1993.

Wormhoudt, J. , M. S. Zahniser, D. D. Nelson, J. B. McManus, R. C. Miake-Lye, and C. E. Kolb, Infrared tunable diode laser diagnostics for aircraft exhaust emissions characterization, Aerodyne Research, Inc., Report ARI-RR-1053, April 1994; also in *Laser Applications in Combustion and Combustion Diagnostics II*, SPIE Proceedings, 2122, 49-60, 1994.

Laboratory Studies of Stratospheric Aerosol Chemistry

Investigator

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Research Objectives

The aim of the task is to investigate the physical chemistry of the sulfuric acid nitric acid hydrogen chloride water system, and to generate and characterize in the laboratory aerosol particles similar to those formed in the high-latitude stratosphere, in order to elucidate the mechanism of formation of polar stratospheric clouds and their chemical reactivity associated with chlorine activation.

Summary of Progress and Results

The freezing behavior of aqueous sulfuric acid solutions has been investigated; the results indicate that in the absence of nitric acid stratospheric sulfate aerosols would not freeze at temperatures above the frost point. The freezing behavior of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ solutions with compositions estimated to correspond to stratospheric aerosols has also been studied; such solutions nucleate more readily. This is a consequence of the very rapid change in composition of the liquid droplets as the temperature drops to within a couple of degrees of the equilibrium temperature at which HNO_3 and H_2O vapors would co-condense to form a liquid solution. This temperature is usually above the frost point – it is around 192-194 K at 100 mbar. A second important consequence of the rapid change in the liquid aerosol composition is the increased HCl solubility, and hence the increased efficiency for chlorine activation.

Publications

Beyer, K. D., S. W. Seago, H. Y. Chang, and M. J. Molina, Composition and freezing of aqueous $\text{H}_2\text{SO}_4/\text{HNO}_3$ solutions under polar stratospheric conditions, *Geophys. Res. Lett.*, **21**, 871, 1994.

Molina, M. J., R. Zhang, P. J. Wooldridge, J. R. McMahon, J. E. Kim, H. Y. Chang, and K. D. Beyer, Physical chemistry of the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ system: Implications for polar stratospheric clouds, *Science*, **261**, 1418, 1993.

Interim Report on Single Particle Analysis Experiment

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Research Objectives

Aerosol particles are crucial to both the chemistry and radiative processes in the lower stratosphere. Heterogeneous chemistry is emerging as perhaps the single most crucial issue in the HSRP assessment. Accurate knowledge of the composition of stratospheric aerosols is fundamental to understanding heterogeneous chemistry. The objective of our research is to build an instrument that can measure the size and composition of individual aerosol particles. The proposal was to build a laboratory instrument with technology suitable for an eventual airborne instrument.

Summary of Progress and Results

We recently completed a successful field trial of our mass spectrometer system for chemical analysis of single aerosol particles. The system was operated at Caribou, CO (altitude 10,200') during September 1993. The site was chosen to take advantage of other measurements available during the informal OH intercomparison there. During the last week of operation (9/23 to 9/29), over 5000 high quality spectra of individual particles were obtained with essentially no adjustments or maintenance to the system.

Shown on the next page is a sequence of successive negative ion spectra taken in just over one minute. Four of the spectra show sulfate as the dominant anion. One of the particles, however, has a completely different spectrum with almost no sulfate at all.

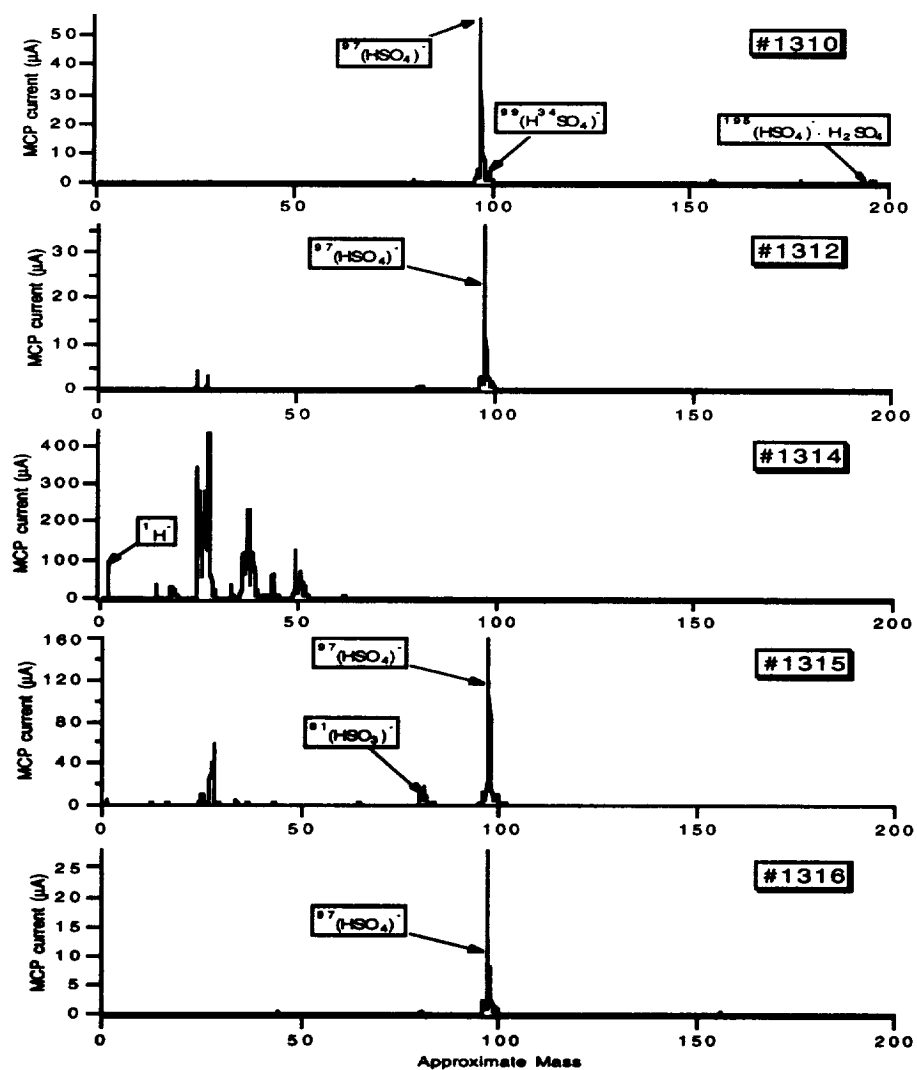


Figure 1. Spectra of 7 successive negative ion spectra taken 930926. #1311 and 1313 were either false triggers or the excimer laser missed the particle.

The composition of the aerosol particles was dramatically different depending on whether there was clean westerly flow or upslope winds from the front range urban corridor. The next figure shows some typical spectra obtained on days with different wind conditions.

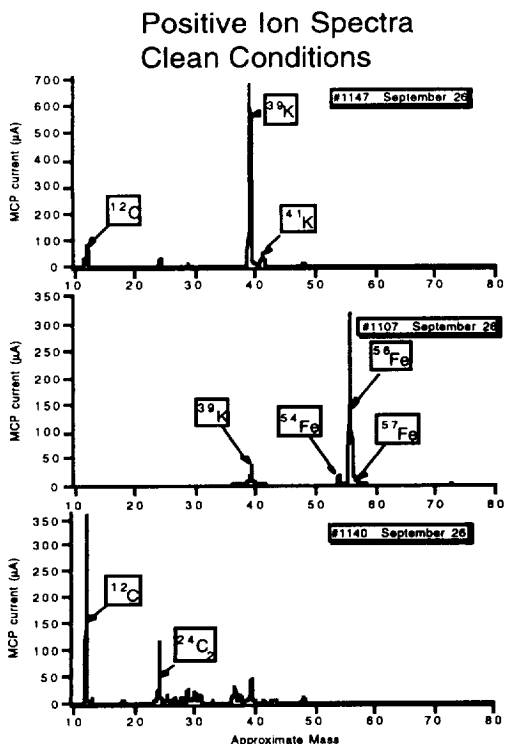


Figure 2. Sample spectra under clean conditions. Spectra are often dominated by inorganic ions. Note: the system is probably more sensitive to potassium than most other species.

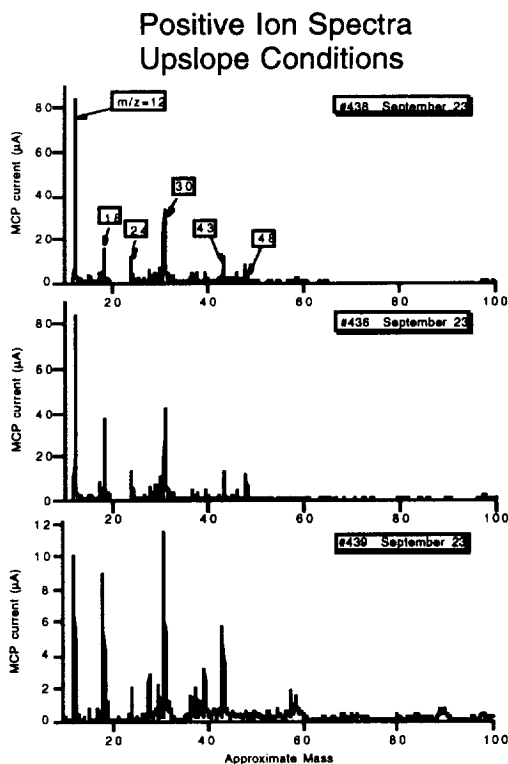


Figure 3. Sample spectra under upslope conditions. Spectra are usually dominated by organic ions. $m/z=12$ is both organic and elemental carbon, $m/z=18$ is ammonium or water, and $m/z=43$ is a common organic fragment ion.

A very simplistic way of compiling what large numbers of spectra are like is just to look at the position of the largest peak, as in the next figure, which shows histograms of two day's data.

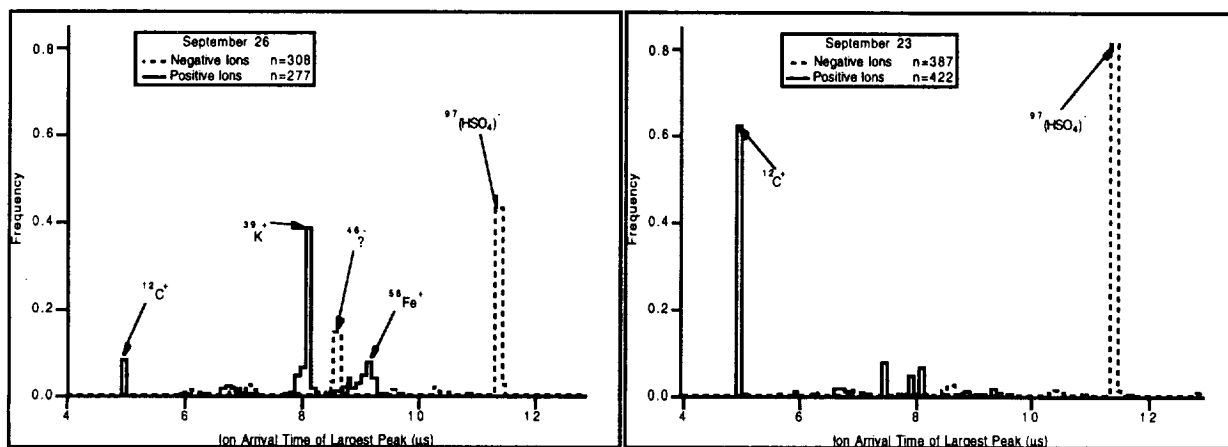


Figure 4. Histograms of largest peaks for clean and upslope conditions.

Note that for the upslope conditions (September 23), simple arithmetic shows that most of the particles must contain considerable amounts of both organic matter and sulfate.

The field tests showed excellent performance for the mass spectrometer system. Further enhancements are planned to provide more accurate sizing of the particles, automatic shutdown procedures to allow unattended operation, application of the focusing inlet work from the University of Minnesota to allow good particle count rates even in the upper troposphere. Extensive laboratory calibrations are also planned. One final figure shows off the kind of signal to noise obtained with the system for a single ambient particle, allowing detection of a boron peak that is much less than 1 percent of the total ion current:

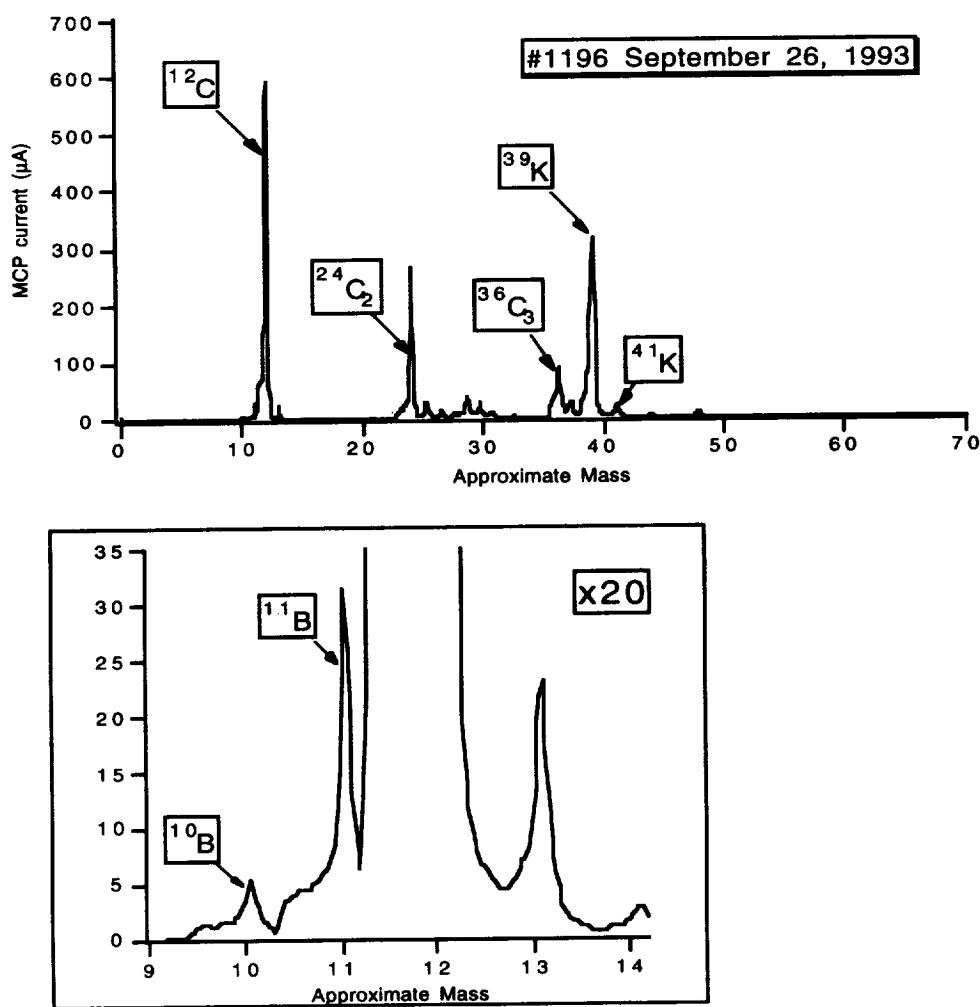


Figure 5. A positive ion spectra of a single ambient particle. The major peaks are carbon clusters and potassium. From the paucity of organic fragment ions, is likely that much of the carbon is elemental. A section is enlarged to show a small pair of boron peaks (with the proper isotopic ratio). Noise is approximately 0.1 μA of microchannel plate (MCP) current so S/N is ≈ 6000 for this spectrum.

Publications

None

Meteorological Analysis for SPADE

Investigators

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Research Objectives

The objective of this work was to provide a variety of meteorological products to SPADE investigators, the science team, and the Project Scientist for flight planning and data analysis purposes. Gridded meteorological observations were captured in near-real time from the National Meteorological Center. From these data, balanced winds and potential vorticity were computed and projected along the flight tracks. Parcel back trajectories were also computed. A high resolution gravity wave model was used to forecast localized turbulence. A radiative transfer code was also used to estimate cooling rates.

Standard data products were produced for use by the mission participants: global analyses along projected flight tracks of the ER-2, curtain files of global analyses track; back trajectories along the flight track; flight meteorological data derived potential vorticity at various isentropic surfaces; reconstructed ozone, nitrous oxide, and chlorine monoxide distribution gravity wave computations, and cooling rate computations.

Summary of Progress and Results

The GSFC group participated in the SPADE test flight series in November 1992 and in April-May 1993. The meteorological products outlined above were routinely provided to the investigators.

Publications

Nash, E., P. A. Newman, J. E. Rosenfield, and M. R. Schoeberl, An objective determination of the polar vortex using Ertel's potential vorticity, submitted to *J. Geophys. Res.*, 1994.

Newman, P. A. *et al.*, Observations of polar vortex fragments in the spring of 1993 at mid-latitudes, in preparation, 1994.

Transport Across Regions With Strong Isentropic Meridional Tracer Gradients: An Investigation Using Existing Lower Stratospheric Aircraft Measurements

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Research Objectives

Our work has two major objectives. The first is to examine the origin and nature of the thin (less than 1 km) layered structures in the tracer fields within the midlatitude lower stratosphere. In particular, we seek to establish the reversibility or irreversibility of these layers, whether they are produced by inertial gravity waves, and the nature and strength of the turbulence which erodes them. The ultimate goal is to show how important or unimportant they are to the overall meridional and vertical transport picture. The second is to extend the description of steep isentropic tracer gradients in the tropics as revealed by recent aircraft and satellite measurements by establishing the relationship to meteorological variables and potential vorticity.

Summary of Progress and Results

Work in 1994 has focused on the first of the two objectives outlined above. We have examined some case studies of inertial gravity waves from the 1986 Spring Midlatitude Field Experiment of the Stratosphere-Troposphere Exchange Project. We have found some dramatic examples of inertial gravity waves in the lower stratosphere located above jet streaks over the eastern Pacific ocean. Though aircraft observations of such phenomena have been analyzed before, the high quality of the meteorological data allows us to characterize the nature of the turbulence embedded in these waves. We found that the turbulence coincided with the regions of minimum Richardson number. Though these regions were statically stable, they tended to be those regions with the minimum vertical potential temperature gradient. As a consequence, preliminary results indicate that the turbulence does not consistently coincide with regions of positive vertical gradients of ozone mixing ratio. This has implications for the proposed role of inertial gravity waves in the vertical turbulent transport of stratospheric and tropospheric trace constituents.

Publications

Pfister, L., and K. R. Chan, Turbulence embedded in inertial gravity waves in the lower stratosphere, in preparation, 1994.

Air Parcel Trajectories in the Lower Stratosphere Using Winds from the "SKYHI" General Circulation Model

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Research Objectives

To investigate the properties of lower stratospheric transport in the high-resolution (1×1.2 degrees) "SKYHI" GCM, by using model-generated winds to generate trajectories of large numbers of trace particles. Of particular interest are transport across the tropopause, across the edge of the polar vortex, and into and out of the tropics.

Summary of Progress and Results

We have developed a sophisticated contour-following technique, to which we refer as "Contour Advection with Surgery" (CAS), to track the two-dimensional motion of material contours. We have used this technique with the SKYHI winds for the southern hemisphere in June (when the wind data are available more frequently from the model) to model transport of air from the Antarctic vortex and its edge on isentropic surfaces (an assumption that limits us to time intervals of 10 days or so). Vigorous wave breaking is clearly taking place in the model at this time. It was found that the simulation of material contour evolution in this active flow was remarkably insensitive to the resolution (in space and time) of the winds. The generation of very fine-scale filaments (widths of less than 1 degree) was almost unchanged when the resolution of the advecting winds was degraded from 1° to 10° . Experiments with tropical and subtropical contours will be run in the near future.

We are currently developing and testing a three-dimensional trajectory code for long-term simulations with the model.

Publications

Waugh, D. W., and R. A. Plumb, Contour advection with surgery: a technique for investigating fine-scale structure in tracer transport, submitted to *J. Atmos. Sci.*, 1993.

Theoretical Studies of the Current Aircraft Fleet's Exhaust in a 3-D Tracer Model and Scattered Radiation Field at Twilight

Investigator

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Research Objectives

This proposal was partially funded with recommendations that the first effort be directed at working with the SPADE measurements and assisting the Canadian CPM team (uv-visible spectrometer). The 3-D simulations of aircraft exhaust with the GISS stratospheric chemical transport model has been delayed.

Summary of Progress and Results

A new photolysis code was developed and delivered for the GUMBO theory model for SPADE. The new documented and standardized numerical method for calculating photodissociation coefficients was been developed at University of California, Irvine. This code has been delivered to the public domain of the GUMBO model for incorporation into the basic trajectory photochemical model for analyzing the SPADE measurements. Accurate simulation of the solar ultraviolet radiation field is essential in determining the chemical partitioning and cycle in the lower stratosphere. The current GUMBO version treats sulfate aerosols as approximately isotropic scatterers with a reduced scattering optical depth. An alternate version of the model which is available as part of SPADE (but not coupled with the GUMBO model) has included a complete Mie scattering code within the photolysis scheme. It can be used to test the accuracy of the assumption of isotropic aerosol scattering (see Zhu and Prather, in preparation, 1994).

This model is currently available to HSRP investigators. In collaboration with Dr. Randy Kawa, this model is being used as a core group (the other being Dr. Kawa's version of Don Anderson's code) that is attempting to resolve differences (one-on-one) and establish a standard result for all photolysis codes that are used in HSRP assessments.

Publications

- Ko, M. K. W., N-D. Sze, and M. J. Prather, Better protection of the ozone layer, *Nature*, 367, 505-508, 1994.
- Prather, M. J., A brief report of interim results from AASE-II with respect to HSRP/AESA studies, Chapter 6, in *The Atmospheric Effects of Stratospheric Aircraft: A Second Program Report*, M. J. Prather and H. L. Wesoky, editors, NASA Reference Publication 1293, 1993.
- Prather, M. J., Lifetimes and eigenstates in atmospheric chemistry, *Geophys. Res. Lett.*, 21, 801-804, 1994.
- Prather, M. J. and E. E. Remsberg, editors, *The Atmospheric Effects of Stratospheric Aircraft: Report of the 1992 Models and Measurements Workshop*, Vol., I, II, and III, NASA Reference Publication 1292, 1993.

Prather, M. J., and R. B. Rood, Credibility of assessment models, Chapter 8, in *The Atmospheric Effects of Stratospheric Aircraft: Interim Assessment Report of the NASA High-Speed Research Program*, R. S. Stolarski and H. L. Wesoky, editors, NASA Reference Publication 1333, 1993.

Zhu, X., and M. J. Prather, The effects of Pinatubo aerosols on photolysis rates in the lower stratosphere during SPADE, in preparation, *Geophys. Res. Lett.*, 1994.

Modeling of the Atmospheric Effects of Stratospheric Aircraft

Investigators

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Research Objectives

To understand and predict the atmospheric effects of a fleet of stratospheric aircraft, using 2-D and 3-D chemical, dynamical, radiative models of the middle atmosphere.

To improve the transport and chemistry formulations in these models and assess the global changes in the atmospheric composition for a variety of scenarios of aircraft emissions.

Summary of Progress and Results

(1) Two-dimensional dynamical and chemical model studies: The NCAR two-dimensional model has been further developed to include the effects of heterogeneous chemistry on sulfate aerosols. The impact of HSCT and CFC injections under these conditions has been studied. We have participated in the recent NASA intercomparison of 2-D models. Further improvements are currently being introduced in the model by including the effects of radiative forcing by aerosols.

We have formulated a detailed microphysical parameterization of the development of aerosols. The parameterization describes the evolution of particles in 25 size bins. The particles in these 25 size bins are also transported in the 2-D model. Transport of 25 extra tracers is far too expensive for use in 3-D models. We are beginning to explore ways of transporting fewer pieces of information without extensively compromising the quality of the simulation, with the goal of modeling transport of aerosols in the 3D model in the future.

Model calculations based on NASA scenarios with and without aerosol chemistry have been presented in Chapter 4, *The Atmospheric Effects of Stratospheric Aircraft: A Third Program Report*, NASA Reference Publication 1313, 1993, and at the Meeting on High-Speed Research Program/Atmospheric Effects of Stratospheric Aircraft.

We will continue to develop the 2-D model and use it to participate in the NASA assessment studies.

(2) Three-dimensional dynamical and chemical model studies: A chemical scheme for the stratosphere has been completed, tested and included in the stratospheric version of the NCAR Community Climate Model. Results obtained by this coupled chemical/radiative/dynamical model have been presented at the High-Speed Research Program/Atmospheric Effects of Stratospheric Aircraft, 1993 Virginia Beach meeting and at the fall meeting of the AGU. The 3-D model simulates the behavior of approximately 30 species belonging to the oxygen, hydrogen, nitrogen, and chlorine families. An off-line version of this model is also completed.

Preliminary simulations of the impact of HSCT have been made with the off-line version of the 3-D model. Simplified 3-D emissions of NO_x and water vapor have been imposed in the lower stratosphere and their effects on the species distribution were calculated.

We continue to develop and validate the 3-D Chemical Transport Model. We now have a baseline, and want to improve the model climatology (both chemistry and dynamical aspects). One of the weakest aspects of our dynamical simulation has been that of the circulation in the south polar regions. We have improved this by modifying the gravity wave drag formulation. Our previous work included only gas phase reactions. We now include heterogeneous reactions occurring on aerosol particles in the 3-D model and have identified their impact on the ozone climatology. We are currently studying the impact of HSCT using the more realistic 3-D emission scenarios developed through the NASA HSRP.

Publications

Rasch, P., B. A. Boville, and G. P. Brasseur: A three-dimensional general circulation model with coupled chemistry for the middle atmosphere, in preparation, *J. Geophys. Res.*

Rasch, P. J, X. X. Tie, B. A. Boville, and D. L. Williamson: A three dimensional transport model for the stratosphere, *J. Geophys. Res.*, 99, 999-1018, 1993.

Tie, X. X. , Potential impact on stratospheric ozone due to emission of hydrocarbon from high altitude aircraft, *Tellus*, in press, 1994.

Tie, X. X., G. P. Brasseur, B. Briegleb, and C. Granier: Two-dimensional simulation of pinatubo aerosol and its effect on stratospheric ozone, submitted to *J. Geophys. Res.*, 1994.

Tie, X. X., G. P. Brasseur, X. Lin, P. Friedlingstein, C. Granier, and P. J. Rasch, The impact of high altitude aircraft on the ozone layer in the stratosphere, *J. Atmos. Chem.*, 18, 103-128, 1994.

Tie, X. X., X. Lin, and G. P. Brasseur: Two dimensional coupled dynamical/chemical/microphysical simulation of global distribution of El Chichon volcanic aerosol, *J. Geophys. Res.*, 99, 16779, 1994.

The Climatic Impact of Stratospheric Aircraft Emissions

Investigators

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Research Objectives

The goal of this research is to explore the potential climatic impact of various stratospheric aircraft emissions including aircraft perturbations to ozone, water vapor, aerosols and cloud condensation nuclei.

Summary of Progress and Results

Because of the possibly small magnitude of "aircraft" climate forcing relative to natural climate variability, it is important to develop accurate knowledge of each of the climate forcings as a function of gas/aerosol amount and knowledge of the relationship between each forcing and the climate model response. We have initiated a systematic study of all the proposed forcings using an efficient sector version of the GISS GCM; in addition, we have made selected studies using the full GISS climate/middle atmosphere model. Results from both sets of studies will be submitted for publication in 1994. Results from the full model are discussed below.

Aircraft ozone and water vapor perturbations are explored in a series of experiments with the GISS climate/middle atmosphere model. Large perturbations to stratospheric ozone and water vapor are investigated, with and without allowing sea surface temperatures to adjust, to illuminate the nature of the dynamic and climatic impact. Then, more realistic ozone and water vapor changes, estimated to result from aircraft emissions, are input, and the equilibrium response obtained.

Removing ozone in the lower stratosphere without allowing sea surface temperatures to change results in lower stratospheric cooling, up to 10° C in the tropical lower stratosphere, with radiative warming about half as large in the middle stratosphere. The temperature changes induce increases in tropospheric and lower stratospheric eddy energy, and in the lower stratosphere residual circulation, on the order of 10 percent. When sea surface temperatures are allowed to respond to this forcing, the global, annual-average surface air temperature cools by about 1° C as a result of the decreased ozone greenhouse capacity, reduced tropospheric water vapor, and increased cloud cover. For more realistic ozone changes as defined in AESA reports, the stratosphere generally cools by a few tenths °C. In this case, the surface air temperature cools by just 0.03° C, due to the conflicting influences of stratospheric ozone reduction and tropospheric ozone increase.

Doubled stratospheric water vapor cools the Middle Atmosphere by 2-3° C and warms the upper troposphere by 0.5° C. Reduced vertical stability leads to increases of tropospheric planetary long wave energy of some 15 percent, and stratospheric residual circulation increases of 5 percent. When sea surface temperatures are allowed to change, the surface air temperature warms by just 0.15° C; the response is muted as the high altitude of energy input minimizes surface level feedbacks, and the upper level cloud cover is reduced. With a "more realistic" increase of stratospheric water vapor of 7 percent, the Middle Atmosphere cools by 0.5° C or less, and the surface also cools, by about 0.2° C; the decrease in high clouds associated with

altered tropospheric stability provides for greater surface cooling than the surface warming due to the stratospheric water vapor increase. Overall, the experiments emphasize how stratospheric changes can affect tropospheric dynamics in the model; how tropospheric changes can affect stratospheric dynamics; and the importance of tropospheric feedback processes when assessing the climatic response to stratospheric perturbations.

Publications

Rind, D. H., and P. Lonergan, Potential climatic and dynamic impacts of stratospheric ozone and water vapor perturbations due to aircraft as modeled in the GISS GCMAM, submitted to *J. Geophys. Res.*, 1994.

Three-Dimensional Transport Studies with Assimilated Meteorological Data: Annual Cycles

Investigator

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Research Objectives

This research effort is closely coordinated with the project headed by Dr. A. Douglass (Two-Dimensional and Three-Dimensional Model Studies of Stratospheric Aircraft Emissions). Both efforts are highly leveraged by the Data Assimilation Office, especially the use of computer resources and the production activities in support of HSRP field missions. The HSRP funding is to improve the long-term fidelity of the winds from the assimilation for use in transport studies and to produce data sets of one year duration or longer. The quality of the winds is evaluated by the transport applications that are validated with satellite, aircraft, and balloon observations.

Summary of Progress and Results

Assimilated Data Products: More than one year of the stratospheric data assimilation, STRATAN, has been completed and the data are available for general usage. Experiments at GSFC show that the data are suitable for transport applications. Data distribution remains problematic, but researchers interested in transferring the data from the GSFC Cray themselves can obtain the data. In addition, limited amounts of the data are available over the Atmospheric Chemistry and Dynamics Branch Data System that supports the ER-2 aircraft missions.

In addition, there are more than five years of data from the GEOS-1 system. This product extends from the ground to 10 hPa with 2 degree latitude by 2.5 degree longitude resolution. Extensive diagnostics have been archived from this system.

ASHOE/MAESA Support: The Data Assimilation Office (DAO) is producing operational analyses and forecasts in support of ASHOE/MAESA. MAESA scientists are relying on the DAO products for flight planning. Both ASHOE and MAESA scientists are using the products for scientific interpretation. The DAO produces both an early and final analysis. The early analysis uses an incomplete input data set, and provides an early product for science planning. The final analysis is produced 12 hours later and has the complete input data set.

Stratosphere/Troposphere Exchange (STE): In collaboration with Dr. A. Douglass studies quantifying STE in synoptic events are underway.

SASS Experiments: Initial transport experiments are underway to assess the impact of the subsonic fleet. Idealized corridor experiments have been run for each season. The purpose of the initial experiments is to understand the bulk properties of transport. Realistic convective transport parameterizations are being developed through non-HSRP mechanisms.

Publications

- Cerniglia, M. C., R. B. Rood, and A. R. Douglass, A three-dimensional simulation of the influence of a cut-off low on the distribution of northern hemispheric processed air in late January 1992, submitted to *J. Geophys. Res.*, 1994.
- Coy, L., R. B. Rood, and P. A. Newman, A comparison of winds from the STRATAN data assimilation system to geostrophic and balanced wind estimates, submitted to *J. Atmos. Sci.*, 51, 2309-2315, 1994.
- Nielsen, J. E., R. B. Rood, A. R. Douglass, M. C. Cerniglia, D. J. Allen, and J. E. Rosenfield, Tracer evolution in winds generated by a global spectral mechanistic model, *J. Geophys. Res.*, 99, 5399, 1994.

Analysis of DC-8 Hydrocarbon and Halocarbon Measurements

Investigators

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Research Objectives

Grab samples collected on board the DC-8 during AASE II yielded approximately 1400 measurements each of 20 halocarbons and more than 30 nonmethane hydrocarbons. Such hydrocarbon and halocarbon measurements can play a key role in investigating the upper troposphere and lower stratosphere.

Summary of Progress and Results

This unique data base, with its wide range of sensitive hydrocarbon and halocarbon measurements in the upper troposphere/lower stratosphere, has been employed to better characterize background conditions for this important atmospheric region.

A rapid decline in the mixing ratios of the shorter lived gases was observed as the aircraft encountered stratospheric or stratospherically influenced air. All of the many stratospheric air samples exhibited reduced hydrocarbon, halocarbon and low chlorofluorocarbon (CFC) concentrations consistent with significant high altitude exposure to UV light.

On two occasions the mixing ratios of NO_x , C_2Cl_4 , C_2H_4 , and numerous other gases were observed to increase near the top of the troposphere, strongly suggesting that the air parcel recently had been augmented with urban air. This illustrates how the co-measurement of tracers such as C_2Cl_4 provide useful information about atmospheric motion and the likely origin of particular air masses.

Publications

- Anderson, B. E., J. E. Collins, G. W. Sachse, G. W. Whiting, D. R. Blake, and F. S. Rowland, AASE II observations of trace carbon species distributions in the mid to upper troposphere, *Geophys. Res. Lett.*, 20, 2539-2542, 1993.
- Weinheimer, A. J., J. G. Walega, B. A. Ridley, B. L. Gary, D. R. Blake, N. J. Blake, F. S. Rowland, G. W. Sachse, B. E. Anderson, and J. E. Collins, Meridional distributions of NO_x , NO_y , and other species in the lower stratosphere and upper troposphere during AASE II, *Geophys. Res. Lett.*, 21, 2583-2586, 1994.

Ames-Moffett Management Support for the Small High-Altitude Science Aircraft (SHASA) Project and the Earth Science Advanced Aircraft (ESAA) Team

Investigators

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Research Objectives

The goal of this task is to increase the probability of success in the SHASA Project to develop Perseus A and to investigate other aircraft developments needed by HSRP/AESA. The approach is to provide limited technical oversight of the SHASA contractor (Aurora Flight Sciences, Inc.) and to perform related studies and services. SHASA is managed by NASA Dryden, which supplies the Project Manager (initially Jennifer Baer-Riedhart, now Walter Sefic). Progress on Perseus A is described in a separate summary by John Langford. This task supplies the SHASA Deputy Project Manager (S. Wegener) and Project Scientist (P. Russell), plus other functions.

Summary of Progress and Results

- Ames hosted monthly ESAA videocons that linked 7 NASA and two DOE sites, for the purpose of reviewing progress on SHASA, the Environmental Research Aircraft & Sensor Technology (ERAST) program, and related needs for and capabilities of advanced aircraft for Earth Science.
- At the request of Mr. Wesoky, Dr. Russell wrote the section on Unmanned Aerospace Vehicles (UAVs) for the HSRP Phase II Program Plan. This section laid the groundwork for the establishment of the ERAST program.
- Mr. Hall conducted simulations of the performance of Perseus A, especially relating to payloads and conditions expected for the field program Measurements for Assessing the Effects of Stratospheric Aircraft (MAESA). He also made preliminary inquiries into the question of FAA regulation of UAV flights, particularly missions needed by current questions in Earth science.
- At the HSRP/AESA Annual Meeting in Virginia Beach, June 6-10, 1993, Dr. Russell and Mr. Richard Christiansen presented the invited talk, The NASA Program in Environmental Research Aircraft & Sensor Technology (ERAST): Programmatic and Determining Scientific Needs. Mr. Wegener presented the invited talk, Perseus for MAESA. Dr. Russell chaired the session.
- Mr. Wegener and Dr. Russell attended a number of meetings at HQ, Dryden, Aurora, and elsewhere to assess progress on SHASA and contribute to the establishment and direction of ERAST.

- At the request of Ms. Baer-Riedhart, Mr. Wegener provided extensive on-site monitoring of Aurora contract performance to enhance communication and coordination between contractor and NASA.

Publications

None

Fast Response Instrumentation for Airborne Measurements of Carbon Monoxide and Methane

Investigators

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Research Objectives

Develop a fast response, high precision instrument to provide *in situ* measurements of carbon monoxide and methane in support of the SASS program.

Summary of Progress and Results

An airborne tunable-diode-laser based CO/CH₄ sensor is currently under development to support the SASS airborne measurement program scheduled for fall 1995. This instrument is designed to make *in situ* measurements on board the NASA DC-8 or similar aircraft to further characterize upper troposphere/lower stratosphere distributions of these species; investigate aircraft corridors for the net effects of air traffic; and, to quantify emission indices during encounters with individual aircraft plumes. Capabilities of this instrument include a time response of less than 0.5 seconds and precision of less than 1 ppbv for CO and less than 2 ppbv for CH₄. The use of gas standards supplied by NOAA/CMDL will assure high accuracy measurements. Previous funding from HSRP supporting our involvement in the AASE-II program has resulted in important contributions to the understanding of this region of the atmosphere most likely to be affected by aircraft emissions. These measurements resulted in substantial enhancement of the CO/CH₄ database for the upper troposphere and lower stratosphere (Anderson *et al.*, 1993; Collins *et al.*, 1993); demonstration that CH₄ is an effective tracer of dynamics in the lower stratosphere (Collins *et al.*, 1993); and, calculated emission indices from aircraft plumes with respect to NO_y (Zheng *et al.*, 1994).

Publications

- Anderson, B. E., J. E. Collins, G. W. Sachse, G. W. Whiting, D. R. Blake, and F. S. Rowland, AASE-II observations of trace carbon species distributions in the mid to upper troposphere, *Geophys. Res. Lett.*, 20, 2539-2542, 1993.
- Collins, J. E., G. W. Sachse, B. E. Anderson, A. J. Weinheimer, J. G. Walega, and B. A. Ridley, AASE-II *in situ* tracer correlations as observed aboard the DC-8; evidence of subsidence and ozone loss, *Geophys. Res. Lett.*, 20, 2543-2546, 1993.
- Zheng, J., A. J. Weinheimer, B. A. Ridley, S. C. Liu, G. W. Sachse, B. E. Anderson, and J. E. Collins, An analysis of aircraft exhaust plumes from accidental encounters, *Geophys. Res. Lett.*, 21, 2579-2582, 1994.

Trajectory Modelling in Support of the High Speed Research Program

Investigators

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Research Objectives

The purpose of these studies is to investigate the dispersion of HSCT emissions, the extent to which emissions build up in flight corridors, and the likelihood of exposure to nitric acid trihydrate (NAT) formation temperatures using the GSFC trajectory model.

Summary of Progress and Results

Preliminary studies were performed which established the validity of the trajectory approach for HSRP assessments and its consistency with other transport approaches. The spatial distribution of parcels calculated with the GSFC trajectory model agrees quite well with the tracer field computed with a 3-D CTM (chemistry and transport model) for the same time period and with similar initialization. The results were also found to be robust with respect to changes in meteorological dataset. Since the interannual study was based on isentropic calculations, the sensitivity to diabatic effects was also investigated and was found to be small on the 3 week time scale of the study.

A series of isentropic trajectory calculations were performed in order to track HSCT emissions released along northern midlatitude oceanic flight corridors. Air parcels were initialized daily along the New York/London and Los Angeles/Tokyo flight paths on the 500 K isentropic surface during the mid-winter period 2-22 January and for each January in the interval 1980-1994. Few parcels emitted along these flight paths at this time of year were found to have experienced NAT formation temperatures, except for the particularly cold Januarys 1986, 1987 and 1992. We also find large zonal fluctuations in the spatial distribution of the emissions. These elevated levels of aircraft emissions must be considered in the interpretation of HSRP assessments based on two-dimensional transport models. Results for an extended 6 month (January-June) period of daily parcel release show that the emission density in the neighborhood of the flight path is 1.5-2 times larger than the zonal average.

Publications

Morris, G. A., M. R. Schoeberl, L. C. Sparling, P. A. Newman, L. R. Lait, L. Elson, J. Waters, A. Roche, J. Kumer, and J. M. Russell, Trajectory mapping of upper atmosphere research satellite (UARS) data, submitted to *J. Geophys. Res.*, 1994.

Schoeberl, M. R., and L. C. Sparling, Trajectory modeling, in diagnostic tools in atmospheric physics, Proceedings of the International School of Physics, Course CXVI, G. Fiocco and G. Visconti, editors, in press, 1994.

Sparling, L. C., M. R. Schoeberl, A. R. Douglass, P. A. Newman, and L. R. Lait, Trajectory modeling of effluent release from lower stratospheric aircraft, submitted to *J. Geophys. Res.*, 1994.

Model and Measurements Data Base for Atmospheric Assessment of Aircraft Effects

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Research Objectives

The purpose of this task is to support the use of model and measurement data sets to understand the effect of aircraft emissions on the atmosphere. The task focuses on compilation, distribution, intercomparison, and maintenance of such data sets in support of AESA studies and of associated workshops and intercomparison activities. Emphasis is on assembling relevant model prediction results and measurement data sets; making them available in an electronic form; and, supporting the intercomparison, manipulation, and display of key parameters. The AESA work is complementary to similar activity funded through the NASA Atmospheric Chemistry Modeling and Analysis Program.

Summary of Progress and Results

A major effort this year has been the publishing of a compact disc (CD) containing the report entitled *The Atmospheric Effects of Stratospheric Aircraft: Report of the 1992 Models and Measurements Workshop* and the data that was submitted to the data base for that report. As a first step, the information to be contained on the CD was made available to users for electronic access. This information included postscript files of the report sections and a set of directories containing the model and measurement data. Several copies of a prototype CD were printed and distributed to test users for review and comment. Based on that review, a final pre-master copy of the CD was developed and released for distribution in the summer of 1994.

Other significant efforts have involved distribution of the aircraft emissions scenario data to the scientific community. A presentation was made at the HSRP/AESA annual meeting describing the data and advertising its' availability. The emissions scenario data sets, color plots of the data, and summary tables were made available to users for electronic access. To date, the data have been provided to more than 25 users from government agencies, universities, and industry. Seasonal aircraft emissions data from McDonnell Douglas have been incorporated into the data base for future reference.

Efforts continue to keep hardware capabilities current. A new color printer has been added to enhance color graphics output capability. Also, the Sun workstations have been upgraded in both memory and processing speed.

Publications

None

Electron Microscope Aerosol Analysis for SPADE

Investigator

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Research Objectives

The goal of this project is to examine the physical and chemical properties of upper tropospheric and lower stratospheric (UT/LS) particles collected during the SPADE missions. The physicochemical characteristics of these particles and their atmospheric residence times will be of importance in determining the potential impacts of aircraft and other aerosol sources on UT/LS radiative balance, cloud/contrail formation, and heterogeneous chemistry.

Summary of Progress and Results

Aerosol samples collected in the midlatitudes by the University of Denver's Multi-sample Aerosol Collection System (MACS) during the SPADE flights in May 1993 have been analyzed using electron microscopy. In the LS samples, >97 percent of the particles showed S and O as the only detectable elements, and from composition and morphology information are believed to be acidic sulfates. These particles showed the characteristic acidic disk pattern, and covered a very large size range of over two orders of magnitude (i.e., ~0.1-10 μm in diameter). In all samples, a mode of sulfate particles of smaller size, which averaged ~0.25-0.50 μm in diameter, were more common than the supermicrometer ones. The vast majority of S-containing disks did not show any solid inclusions larger than the detection limit of ~0.03 μm . Infrequently-observed nonsulfate materials included soot carbon, other C-rich particles (some with metallic portions), and solid particles with crustal-type components. These nonsulfate particles from the LS usually showed a S-rich coating as a residue around the particle or as a S signal in the x-ray spectrum. Samples collected very near and just below the midlatitude tropopause also showed sulfates to be the most prevalent particle type. The fraction of sulfate particles in the UT averaged 91-94 percent of the total particle concentration. Differences in the morphologies of impacted sulfate particles suggests an acidity gradient across the tropopause, with higher acidity in the LS. Nonsulfate particles observed in the UT samples included crustal-type materials, hydrated marine salts, carbon-rich particles of several types, and metal-containing particles of uncertain origin. Most of these UT particles were not coated with detectable quantities of sulfate.

Publications

Sheridan, P. J., C. A. Brock, and J. C. Wilson, Aerosol particles in the upper troposphere and lower stratosphere in midlatitudes. I: Elemental composition and morphology of individual particles, *Geophys. Res. Lett.*, 21, 2587-2590, 1994.

Heterogeneous Chemistry Related to Stratospheric Aircraft

Investigator

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Research Objectives

We are performing laboratory experiments aimed at characterizing thin films representative of stratospheric aerosols. In particular, we are studying $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ films representative of the global stratospheric sulfate layer and nitric acid/ice films representative of type I polar stratospheric clouds (PSCs). We hope to understand the microphysical properties of these aerosols so that heterogeneous chemical effects can be properly included in atmospheric models of high speed civil transports.

Summary of Progress and Results

Type I PSCs are thought to nucleate and grow on stratospheric sulfate aerosols (SSAs). To model this system, we exposed thin sulfuric acid films to water and nitric acid vapors while slowing cooling. FTIR spectroscopy was used to probe the phase of the sulfuric acid and to identify the $\text{HNO}_3/\text{H}_2\text{O}$ films that condensed as a function of saturation ratio, S . We found that for $S_{\text{NAT}} \geq 28$, crystalline nitric acid trihydrate (NAT) grew on crystalline sulfuric acid tetrahydrate (SAT) and also on supercooled sulfuric acid films. Current experiments are probing the system at lower S values.

Other recent studies used optical interference techniques to examine the real refractive index at $\lambda = 632 \text{ nm}$ for $\text{HNO}_3/\text{H}_2\text{O}$ films representative of type I PSCs. Refractive indices were measured for both amorphous and crystalline $\text{HNO}_3/\text{H}_2\text{O}$ films. For the amorphous films, the refractive indices increased with increasing nitric acid content. The values ranges from $n = 1.31$ for pure ice to $n = 1.47$ for nearly pure nitric acid. A Lorentz-Lorenz analysis was in good agreement with the measured indices. Indices for crystalline $\text{HNO}_3/\text{H}_2\text{O}$ films were substantially higher than for the amorphous analogs.

Publications

- Berland, B. S., D. R. Haynes, K. L. Foster, M. A. Tolbert, S. M. George, and O. B. Toon, Refractive indices of amorphous and crystalline $\text{HNO}_3/\text{H}_2\text{O}$ films representative of polar stratospheric clouds, *J. Phys. Chem.*, in press, 1993.
- Iraci, L. T., A. M. Middlebrook, M. A. Wilson, and M. A. Tolbert, Growth of nitric acid hydrates on thin sulfuric acid films, *Geophys. Res. Lett.*, 21, 867-870, 1994.
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Heterogeneous Chemistry and Microphysical Modeling and Analysis in Support of the HSRP

Investigators

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Research Objectives

The objectives of this research are to maximize the science return from the AASE-II mission; to study heterogeneous reactions on volcanic aerosols and transport of volcanic aerosols; and, to provide data useful for determining the properties of polar stratospheric clouds.

Summary of Progress and Results

The DC-8 aircraft was successfully flown in the 1992 AASE-II program. As the flight scientist for the DC-8, I served as the co-editor of a Geophysical Research Letters special issue to ensure that data relevant to HSRP were made available in a timely way. I also prepared a paper for Science on heterogeneous chemical conversions on volcanic sulfuric acid aerosols using data from the DC-8 flights in AASE-II. I published studies of the transport of Pinatubo material during the first few months after the eruption. These studies show that radiative heating in the cloud induced important changes in the stratospheric circulation. Further, the data provide a test bed for models of stratospheric transport. Finally, working with Professor Tolbert at the University of Colorado, I obtained the refractive indices of a number of materials, such as nitric acid trihydrate, that are thought likely to compose polar stratospheric clouds. These refractive indices should enable remote observations of the clouds to be interpreted in terms of the composition of the clouds.

Publications

Anderson, J. G., and O. B. Toon, Airborne Arctic Stratospheric Expedition II: An overview, *Geophys. Res. Lett.*, 20, 2499-2502, 1993.

Berland, B., K. Foster, S. George, D. Haynes, M. A. Tolbert, and O. B. Toon, Optical characterization of model polar stratospheric clouds: Refractive indices of amorphous and crystalline HNO₃/H₂O films, *J. Physical Chem.*, in press, 1994.

Toon, O. B., E. V. Browell, B. Gary, J. Jordan, L. R. Lait, P. A. Newman, R. F. Pueschel, P. B. Russell, M. R. Schoeberl, H. B. Selkirk, G. C. Toon, W. A. Traub, and F. P. J. Valero, Heterogeneous reaction probabilities, solubilities, and physical state of cold volcanic aerosols, *Science*, 261, 1136-1140, 1993.

Toon, O. B., B. G. Koehler, J. Jordon, A. M. Middlebrook, and M. A. Tolbert, Infrared optical constants of H₂O ice, amorphous nitric acid solutions, and nitric acid hydrates, *J. Geophys. Res.*, 99, 25631-25654, 1994.

Young, R. E., H. Houben, and O. B. Toon, Radiatively forced dispersion of the Mt. Pinatubo volcanic cloud and induced temperature perturbations in the stratosphere during the first few months following the eruption, *Geophys. Res. Lett.*, 21, 369-372, 1994.

Measurements and Interpretation of Total Reactive Nitrogen, Nitric Oxide, Water Vapor and Ozone in the Lower Stratosphere

Investigators

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Research Objectives

- Acquire observations of NO, NO_y, H₂O and O₃ during the SPADE and ASHOE/MAESA missions
- Analyze these data as unified set with those obtained on earlier ER-2 missions: STEP, AAOE, AASE and AASE-II
- Perform photochemical modelling studies to compare with the observations
- Intercompare observations of those HALOE species (NO, NO₂, CH₄, H₂O, O₃, HCl) with those which are also measured on the ER-2

Summary of Progress and Results

- Observations of NO, NO_y, H₂O, O₃ and on some flights of NO₂ were obtained during SPADE and during the first phase of ASHOE/MAESA (the remaining 3 phases are still in the future at the time of writing)
- Data analysis is in progress; certain results are apparent and have been written up
- Photochemical modelling studies are at an early stage
- Intercomparisons have been made between the ER-2 and HALOE, and are being redone as the airborne missions continue and HALOE retrieval algorithms evolve

Publications

Fahey, D. W., S. R. Kawa, E. L. Woodbridge, P. Tin, J. C. Wilson, H. H. Jonsson, J. R. Dye, D. Baumgardner, S. Borrmann, D. W. Toohey, L. M. Avallone, M. H. Proffitt, J. Margitan, M. Loewenstein, J. R. Podolske, R. J. Salawitch, S. C. Wofsy, M. K. W. Ko, D. E. Anderson, M. R. Schoeberl, and K. R. Chan, *In situ* measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion, *Nature*, 363, 509, 1993.

Kawa, S. R., and D. W. Fahey *et al.*, Interpretation of NO_x/NO_y observations from AASE-II using a model of chemistry along trajectories, *Geophys. Res. Lett.*, 20, 2507, 1993.

- Kelly, K. K., M. H. Proffitt, K. R. Chan, M. Loewenstein, J. R. Podolske, S. E. Strahan, J. C. Wilson, and D. Kley, Water vapor and cloud water measurements over Darwin during the STEP 1987 tropical mission, *J. Geophys. Res.*, 98, 8713-8723, 1993.
- Murphy, D. M., D. W. Fahey, M. H. Proffitt, S. C. Liu, K. R. Chan, C. S. Eubank, S. R. Kawa, and K. K. Kelly, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, 98, 8751, 1993.
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- Russell, J. M. III, A. F. Tuck, L. L. Gordley, J. H. Park, S. R. Drayson, J. E. Harries, R. J. Cicerone, and P. J. Crutzen, HALOE Antarctic observations in the spring of 1991, *Geophys. Res. Lett.*, 20, 719, 1993.
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- Tao, X., and A. F. Tuck, On the distribution of cold air near the vortex edge in the lower stratosphere, *J. Geophys. Res.*, 99, 3431, 1994.
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- Tuck, A. F., S. J. Hovde, K. K. Kelly, J. M. Russell III, C. R. Webster, and R. D. May, Intercomparison of HALOE and ER-2 aircraft H₂O and CH₄ observations collected during the second Airborne Arctic Stratospheric Experiment (AASE-II), *Geophys. Res. Lett.*, 20, 1243, 1993.

On the Strength of Brewer-Dobson Circulation and Other Strat-Trop Exchange Processes

Investigators

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Research Objectives

To quantify the strength of the mass transport across the tropopause, and to develop direct and indirect means to validate its strength, in support of the HSRP goal of assessing the impact of stratospheric aircrafts.

Summary of Progress and Results

We have continued our study of year-to-year variation of mass circulation in the lower stratosphere. In particular, we are focusing on the difference in mass transports between the easterly and the westerly phases of the QBO. The observed variation of total ozone is used to infer and quantify the strength of the circulation difference.

Publications

Tung, K. K., and H. Yang, 1994: On global QBO in circulation and ozone, Part I: Reexamination of observational evidence, *J. Atmos. Sci.*, *51*, 2699-2707, 1994.

Tung, K. K., and H. Yang, 1994: On global QBO in circulation and ozone, Part II: A simple mechanistic model, *J. Atmos. Sci.*, *51*, 2708-2721, 1994.

Modeling the Atmospheric Effects of Stratospheric Aircraft

Investigators

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Research Objectives

- 1) Effects of the changing atmospheric composition on the aircraft impact
- 2) Interactions of physical/chemical heterogeneous processes
- 3) Feedback of aircraft emissions on the aerosol load

Summary of Progress and Results

The research activity, during the last year, has focused primarily on modeling the aerosol interactions with the chemical balance of the lower stratosphere. To this end, we have first implemented a photochemical two-dimensional (2-D) model with a microphysics code for aerosol formation and growth. A gas-particle interaction term is included in the continuity equations for sulfuric acid, nitric acid, and water vapor. Then, we have studied the effects of HSCT emissions in the 2-D framework in the presence of different classes of stratospheric aerosols. Feedback mechanisms of gas injection from the aircraft on the aerosol surface density are included.

Another study has been conducted on the possible changes of the aircraft impact due to modifications of the stratospheric radiative balance induced by perturbations of greenhouse gases. We have focused on the CO₂ increase predicted for the next century, that is, when HSCT should be operational. For this purpose, we have first used a three-dimensional model for the radiative and dynamical calculations, and then, the 2-D model. The denitrification associated with the formation of nitric acid trihydrate (NAT) aerosols is shown to significantly affect the partition of chemical families. The radiative perturbation introduced by the CO₂ increase is found to affect the stratospheric dynamics in such a way that the lower stratospheric residual circulation is enhanced. This has the effect to reduce by about 15 percent the stratospheric residence time of odd nitrogen injected by the aircraft, so that the overall perturbation of stratospheric chemistry, due to HSCT, is mitigated with respect to the reference case in which CO₂ is kept at the present level. Another important effect is found to be produced by the stratospheric temperature cooling following the CO₂ increase. The enhancement of the surface area density of NAT aerosols causes a larger denitrification, which in turn, produces a further decrease of the relative role of the NO_x catalytic cycle for ozone destruction. For this reason, a global ozone increase is found in the case of 500 ppmv CO₂ (+ 0.30 percent for Mach 2.4 and NO_x-EI = 15), while the balance between the different tendencies of ClO, NO_x, and OH cycles is found to be closer in the reference case of 335 ppmv CO₂ (-0.35 percent for global ozone).

Publications

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- Pitari, G., and G. Visconti, Possible effects of CO₂ increase on the HSCT impact on ozone, *J. Geophys. Res.*, 99, 16879, 1994.
- Pitari, G., S. Palermi, and G. Visconti, Impact on ozone of high speed stratospheric aircraft: Effects of the emission scenario, *Ann. Geophysicae*, in press, 1994.

Aircraft Laser Infrared Absorption Spectrometer (ALIAS-II) for N₂O, CH₄, and H₂O Profiles from Perseus; and HCl, HNO₃, NO₂, N₂O, and CH₄ Measurements from ALIAS-I on the ER-2

Investigators

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Research Objectives

In situ measurements of HCl, N₂O, CH₄, H₂O, NO₂, and HNO₃ will be used in conjunction with other simultaneous measurements from the ER-2 and from Perseus to define the reference state of the atmosphere in the altitude region 10-30 km. These measurements will constrain model simulations which will assess the impact of a proposed fleet of supersonic aircraft on stratospheric ozone.

Specific objectives over the next year are to complete the build of the ALIAS-II spectrometer for measurement of H₂O, CH₄, and N₂O during Perseus test flights in 1994; and, to fly ALIAS-I on the ER-2 for measurements of HCl, N₂O, CH₄, NO₂, and CO during the ASHOE/MAESA campaign of 1994.

Summary of Progress and Results

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument was successfully flown in the SPADE Parts I and II flight series out of California, producing the first measurements of NO₂ and its diurnal variation, measurements of HCl, N₂O, and CH₄. The data have allowed a study of the effects of heterogeneous processing on NO₂, and the degree to which photochemical models predict the measured NO₂/NO ratio, when, for the first time, simultaneous measurements of NO₂, NO, O₃, HO₂, and ClO were made on the SPADE payload. The HCl vs. N₂O data-base has been extended to support the earlier ALIAS measurements of HCl. Since the SPADE flight series, ALIAS (ER-2) has undergone numerous modifications designed to improve reliability (principally) and performance for the ASHOE/MAESA campaign, in which ALIAS will provide simultaneous measurements of the tracers N₂O, CH₄, and CO, and of HCl and NO₂.

The build of the Aircraft Laser Infrared Absorption Spectrometer (ALIAS-II) instrument for Perseus is well underway. All the ALIAS-II electronics are in-house, tested and under final assembly, lasers are selected and tested, the two-channel dewar is in-house and tested. ALIAS-II diode lasers for H₂O, N₂O, and CH₄ in the flight dewar have been directed to the multi-component retroreflector assembly and returned to the flight detectors, in a final laboratory demonstration to finalize the steering optical component selection. Fabrication of the mechanical modular assemblies remains to be done.

Publications

Jaegle, L., C. R. Webster, R. D. May, D. W. Fahey, E. L. Woodbridge, E. R. Keim, R. S. Gao, M. H. Proffitt, R. M. Stimpfle, P. O. Wennberg, R. J. Salawitch, S. C. Wofsy, and L. Pfister, *In situ* measurements of the NO₂/NO ratio for testing atmospheric photochemical models, *Geophys. Res. Lett.*, 21, 2555-2558, 1994.

- May, R. D., C. R. Webster, and L. Jaegle, New measurements of NO₂ for testing the heterogeneous hydrolysis of N₂O₅ on sulfate aerosols, in preparation, *Geophys. Res. Lett.*, SPADÉ special issue, 1994.
- Webster, C. R., R. D. May, L. Jaegle, H. Hu, S. P. Sander, M. R. Gunson, G. C. Toon, J. M. Russell III, R. M. Stimpfle, J. P. Koplow, R. J. Salawitch, and H. A. Michelson, Hydrochloric acid and the chlorine budget of the stratosphere, *Geophys. Res. Lett.*, 21, 2575-2578, 1994.

NO, NO₂, NO_y, and O₃ Measurements During the Arctic DC-8 1992 Missions

Investigators

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Research Objectives

(1) To reduce and archive NO, NO₂, NO_y, and O₃ data obtained from the DC-8 in AASE II. (2) To determine the distribution of NO, NO₂, and NO_y, in conjunction with O₃, in the lower stratosphere and upper troposphere of the wintertime Northern Hemisphere. (3) To look for the effects of NO_x emissions from present-day aircraft. (4) To study effects of wintertime polar chemistry on air at DC-8 altitudes.

Summary of Progress and Results

(1) Our measurements are archived on the 2nd edition of the AASE II CDROM.

(2) In Weinheimer *et al.* (1994), we present meridional distributions of NO_x, NO_y, and other species. In the lowest few km of the stratosphere there is little vertical gradient in NO_x. There is a substantial latitudinal gradient, with 50 pptv above the pole and 120 pptv near 40N. In the uppermost few km of the troposphere, background values range from 30 pptv over the pole to 90 pptv near 40N. On two occasions higher values, up to 140 pptv in the mean, were seen 2-3 km below the tropopause in association with frontal systems. The meridional distributions of CO, C₂Cl₄, and n-C₅H₁₂ show the same feature, suggesting that the source of the elevated NO_x is near the earth's surface. In the stratosphere at higher latitudes (50-90N), the NO_x/NO_y ratio increases from ~3 to ~8 percent as the tropopause is approached from above.

(3) In Zheng *et al.* (1994), we summarize measurements of 20 exhaust plume crossings where the NO_y increment was 1 ppbv or greater. For one of these, there were associated increments in both CO and CO₂. For four others, there were increments in CO₂. Atmospheric variability in CO and CO₂, plus less than desirable time response in their measurement, made it difficult to unambiguously assign CO and CO₂ increments to the readily identifiable NO_y spikes. Nonetheless we were able to infer ratios of emission indices among the different species. The NO_y/CO₂ ratio compares well with published subsonic emission indices. The ratios suggest that the NASA CO emission index may be low by a factor of 5. Also, we conclude that odd nitrogen other than NO_x accounts for a very small percentage of the emitted odd nitrogen.

(4) In Folkins *et al.* (1993), we compare the measured NO_x/NO_y ratio to that computed in a 3-D semi-Lagrangian chemistry/transport model, with and without the inclusion of heterogeneous reactions. The comparison shows that inclusion of the N₂O₅ aerosol reaction generally improves the agreement, but that it often makes the ratio too low.

Publications

Collins, J. E., G. W. Sachse, B. E. Anderson, A. J. Weinheimer, J. G. Walega, and B. A. Ridley, AASE-II *in situ* tracer correlations of methane, nitrous oxide, and ozone as observed aboard the DC-8, *Geophys. Res. Lett.*, 20, 2543-2546, 1993.

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- Weinheimer, A. J., J. G. Walega, B. A. Ridley, B. L. Gary, D. R. Blake, N. J. Blake, F. S. Rowland, G. W. Sachse, B. E. Anderson, and J. E. Collins, Meridional distributions of NO_x , NO_y , and other species in the lower stratosphere and upper troposphere during AASE II, *Geophys. Res. Lett.*, 21, 2583-2586, 1994.
- Weinheimer, A. J., J. G. Walega, B. A. Ridley, G. W. Sachse, B. E. Anderson, and J. E. Collins, Stratospheric NO_y measurements on the NASA DC-8 during AASE II, *Geophys. Res. Lett.*, 20, 2563-2566, 1993.
- Zheng, J., A. J. Weinheimer, B. A. Ridley, S. C. Liu, G. W. Sachse, B. E. Anderson, and J. E. Collins, An analysis of aircraft exhaust plumes from accidental encounters, *Geophys. Res. Lett.*, 21, 2579-2582, 1994.

Investigation of Combustion Aerosols as a Potential Sink for NO_x in the Expanding Exhaust Plume of the HSCT

Investigators

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Research Objectives

- (1) The development of a database to characterize carbonaceous aerosols generated in laboratory burners operating on typical jet fuels. The specific properties examined were typical concentrations, size distributions and growth of hydration.
- (2) To demonstrate a method for determining accommodation coefficients for NO and NO₂ on well defined jet fuel-generated carbonaceous aerosol.

Summary of Progress and Results

- (1) The UMR cloud simulation chamber continued to be configured for the proof of principle accommodation coefficient experiments tasked for year 2 as described in the 1993 research summary. Data have been gathered on the accommodation coefficient of NO₂ and are currently being evaluated for disclosure at the forthcoming AESA annual review in June 1994.
- (2) The UMR/MDA team and their MASS have joined the EEC sponsored POLINAT program led by DLR (Oberpfaffenhofen) in Germany. The UMR MASS derives many of its capabilities from the excellent database generated under this NASA research task. The data from the proof of principle flights campaigns in 1993 will be presented at the International Scientific Colloquium on the Impact of Emissions from Aircraft and Space-Craft upon the Atmosphere in Cologne, Germany, April 18-20, 1994.
- (3) The measurements performed under an independent research project funded by the McDonnell Douglas Corporation combined with those made during this research task have led to the determination for preliminary particulate emission indices for the 404 engine. These data will also be presented at the forthcoming AESA annual review in June 1994. The results of this study are being shared with G. E. who are currently tasked with generating a model to predict such indices.

Publications

Particulate characterization in the near field of commercial transport aircraft exhaust plumes using the UMR-MASS, International Scientific Colloquium on the Impact of Emissions from Aircraft and Space-Craft upon the Atmosphere, Cologne, Germany, April 18-20, 1994.

Particulates and aerosols characterized in real time from harsh environments using the UMR mobile aerosol sampling system (MASS), AIAA Sponsored Joint Propulsion Conference and Exhibit, Monterey, CA, June 28 - July 1, 1993.

Scavenging on carbonaceous aerosol surfaces in aircraft exhaust plumes, AIAA Sponsored Joint Propulsion Conference and Exhibit, Monterey, CA, June 28 - July 1, 1993.

Detection and Analysis of Aircraft Produced Particles During SPADE

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Research Objectives

The Stratospheric Photochemistry, Aerosol and Dynamics Expedition (SPADE) occurred in spring of 1993. In SPADE, we operated two instruments. With the Condensation Nucleus Counter II (CNCII), we measured condensation nuclei (CN) with two sensors and collected aerosol samples with the Multiple Sample Aerosol Collection System (MACS). One CN sample stream was heated to temperatures of 200° C and the second sample stream was not heated. Previous work shows that sulfuric acid particles vaporize at the temperatures of the heater. The Focused Cavity Aerosol Spectrometer (FCAS) measures size distributions in the 0.07 to 1 micron size range. By subtracting the number concentration measured by the FCAS from those measured from the CNC, it is possible to estimate the number of particles in the 0.01 to 0.07 micron range.

Summary of Progress and Results

Since the last report, we have finished the measurements in SPADE, reduced the data, and submitted it to the data archive. The data analysis for SPADE included supporting the analysis of the collected impactor samples by Pat Sheridan. We selected grids which permitted the composition and gradients in composition of particles near the mid-latitude tropopause to be the results of this analysis which are reported in Sheridan *et al.* (1994). Sulfate particles were found to dominate the tropopause region. A small fraction of the particles were characterized by crustal, metallic and carbonaceous composition. The gradients in the non-sulfate particles were strong in the vicinity of the tropopause.

In SPADE, the ER-2 crossed its own wake several times and CN provided a clear marker for the plume. Papers, which describe the ER-2 exhaust, are being prepared (Fahey *et al.*, and Brock *et al.*). The SPADE flights also permitted the evolution of the aerosol resulting from the eruption of Mt. Pinatubo to be followed. This evolution is also being described.

Publications

Brock, C. A., H. H. Jonsson, and J. C. Wilson, Measurements of particle concentration and volatility in the exhaust of a stratospheric aircraft, in preparation.

Fahey, D. W., E. Keim, E. L. Woodbridge, R. S. Gao, K. A. Boering, B. C. Daube, S. C. Wofsy, E. Hintsa, C. A. Brock, J. C. Wilson, R. P. Lohmann, R. C. Miake-Lye, M. Loewenstein, M. H. Proffitt, R. M. Stimpfle, S. W. Bowen, and K. R. Chan, Observations of aircraft exhaust in the lower stratosphere: The emission index of reactive nitrogen oxide species, in preparation.

Jonsson, H. H., J. C. Wilson, and C. A. Brock, Evolution of the concentration and size of the stratospheric aerosol following the eruption of Mt. Pinatubo, in preparation.

Sheridan, P. J., C. A. Brock, and J. C. Wilson, Aerosol particles in the upper troposphere and lower stratosphere: Elemental composition and morphology of individual particles in northern midlatitudes, *Geophys. Res. Lett.*, 21, 2587-2590, 1994.

Aerosol Measurements From the ER-2 in SPADE II and ASHOE/MAESA: Upgrade of the Focused Cavity Aerosol Spectrometer and its Sampling Inlet

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Research Objectives

The objective of this task was to prepare a Focused Cavity Aerosol Spectrometer (FCAS) for use in ASHOE/MAESA. It was decided to build a new instrument and the following tasks were undertaken:

1. An optics block consisting of laser, passive cavity, detectors and laser power supplies was obtained from Particle Measuring Systems in Boulder
2. A pulse analysis card and data acquisition system were acquired from NCAR in Boulder
3. The instrument case was designed and constructed
4. An aerosol injection and flow system was designed and constructed
5. The power supplies and aircraft connections were provided
6. The instrument design was accepted by NASA and Lockheed
7. The instrument was constructed, integrated onto the ER-2 aircraft, and flown in test flights
8. The instrument has been calibrated and is being operated in ASHOE/MAESA

The FCAS data system also serves as the data system for the NCAR Multiple Angle Scattering Probe (MASP).

Publications

None

High-Altitude NO and NO_y Measurements Using a New Lightweight Chemiluminescence Instrument

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Research Objectives

To develop, test, and perform stratospheric measurements with a lightweight, dual-channel sensor for NO and NO_y. Although this instrument is being designed for the Perseus A aircraft, its compact size, light weight, and low power consumption will allow it to be flown on other platforms. The design will allow measurements over a wide range of altitudes, up to 30 km.

Summary of Progress and Results

In the past year, we have finalized the instrument layout and specified key components. Considerable effort was directed towards identification or design of parts that best meet the stringent weight, space, and power requirements of the aircraft. Many of these components have been fabricated and they are currently being tested. We have begun the final design phase which includes the ground-support apparatus.

Laboratory testing has focused on two aspects of the detection scheme:

(1) Chemiluminescent detection of NO via reaction with O₃. We have designed a new NO chemiluminescence cell that provides high sensitivity (10 counts/ppt/s) and significantly reduces the "zero artifact," even at low pressures. This cell weighs 0.54 kg, 65 percent lighter than the previous cell. The NO detection scheme was further optimized by careful choice of PMT, photon counter, and cell coating. We have constructed and tested a very efficient, reliable, and lightweight ozonizer.

(2) Catalytic conversion of NO_y to NO. We have performed tests of catalyst efficiency using both NO₂ and isopropyl nitrate over a wide range of temperatures, pressures, and H₂ flow rates for both pure and alloy gold. These tests are on-going and will determine the optimum conditions under which to operate the flight instrument for a wide range of altitudes. We have tested an NO₂ titration source that will be used for in-flight calibration.

Publications

Dessler A. E., R. M. Stimpfle, B. C. Daube, R. J. Salawitch, E. M. Weinstock, D. M. Judah, J. D. Burley, J. W. Munger, S. C. Wofsy, J. G. Anderson, M. P. McCormick, and W. P. Chu, Balloon-borne measurements of ClO, NO, and O₃ in a volcanic cloud: An analysis of heterogeneous chemistry between 20 and 30 km, *Geophys. Res. Lett.*, 20, 2527, 1993.

Stratospheric Sulfur Oxidation Kinetics

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Research Objectives

The purpose of this study is to determine the mechanisms and chemical kinetics rate parameters controlling the homogeneous and heterogeneous oxidation of SO_2 to H_2SO_4 in high-altitude aircraft plume/wakes and in the ambient stratosphere.

Summary of Progress and Results

We have designed a series of fast-flow tube experiments to measure the temperature dependent rate of the homogeneous reaction of the SO_3 molecule with H_2O vapor to form H_2SO (v). These kinetics are studied in a novel, high-pressure turbulent fast-flow reactor, previously designed and fabricated at Massachusetts Institute of Technology which minimizes heterogeneous loss of SO_3 (reacting with H_2O) on reactor walls. Reactants and products are detected via an atmospheric pressure chemical ionization mass spectrometer (APCIMS) which is coupled to the exit of the flow reactor. Chemical ionization occurs via charge transfer of either reagent ions (SF_6^-) or electrons, which are generated in a corona discharge of the appropriate neutral species.

Preliminary results for the reaction $\text{SO}_3 + \text{H}_2\text{O}$ show a strong negative temperature dependence on the observed decay rate of SO_3 in the presence of excess water vapor. The measurements yield an observed rate constant of $k = 5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ at 50°C . This negative temperature dependence implies that the $\text{SO}_3 \cdot \text{H}_2\text{O}$ adduct species may be reacting. Measurements performed at 21°C show SO_3 decay to be second order with respect to the water vapor concentration, consistent with the dimer reaction channel, i.e. $\text{SO}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$. The possibility of a parallel reaction pathway, $\text{SO}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$, also second order in $[\text{H}_2\text{O}]$ is not ruled out. More extensive temperature dependent studies are being performed and a model is being developed to elucidate this possible dual reaction mechanism.

Publications

None

Heterogeneous Chemistry Related to Stratospheric Aircraft Emissions

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Research Objectives

A laboratory program is investigating the heterogeneous chemistry of stratospheric aerosols, composed of mixtures of H_2SO_4 , HNO_3 , HCl and H_2O . The project has two tasks: thermodynamics, i.e., measurements of aerosol vapor pressures and composition under simulated stratospheric conditions; and, kinetics, i.e., measurements of the rates of uptake and reaction of gaseous species such as N_2O_5 , HCl , HNO_3 , ClONO_2 , and CH_2O on aerosol droplets.

Summary of Progress and Results

(1) Nitric acid hydrate formation has been studied by measuring vapor pressures of H_2O and HNO_3 over ternary liquid samples of H_2SO_4 , HNO_3 , and H_2O . Initial nitric acid solid condensation involves a newly identified mixed hydrate (MixH) of composition $\text{H}_2\text{SO}_4 \cdot \text{HNO}_3 \cdot 5\text{H}_2\text{O}$. MixH formation is followed by formation of metastable $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ (nitric acid dihydrate, NAD), which can persist for days before forming more stable $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (nitric acid trihydrate, NAT). Overall, the sequence of solid phase formation obeys Ostwald's rule which predicts initial formation of less stable phases. Such a sequence can explain differential growth of HNO_3 rich particles (e.g., via $\text{NAD} \rightarrow \text{NAT}$ conversion). The sedimentation of such large particles can lead to stratospheric denitrification.

(2) HCl , N_2O_5 , and ClONO_2 uptake rates into cold $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ droplets (40-70 wt%, down to 230 K) have been determined. Results for HCl solubility and N_2O_5 and ClONO_2 reactivity with H_2O agree well with results from other laboratories. The reactivity of N_2O_5 and ClONO_2 peak at $T = \sim 230$ K, likely indicative of a liquid diffusion limited reaction mechanism. Combined with results from other groups, this temperature dependence is important for extrapolation of heterogeneous rates to stratospheric sulfuric acid aerosols at polar temperatures ≤ 200 K.

Publications

Fox, L. E., D. R. Worsnop, M. S. Zahniser, and S. C. Wofsy, Non-equilibrium phases in polar stratospheric aerosols, submitted to *Science*.

Robinson, G. N., D. R. Worsnop, M. S. Zahniser, C. E. Kolb, and P. Davidovits, Heterogeneous reaction probabilities of N_2O_5 and ClONO_2 on cold 39 to 69 percent sulfuric acid droplets, submitted to *J. Phys. Chem.*

Worsnop, D. R., L. E. Fox, M. S. Zahniser, and S. C. Wofsy, Vapor pressures of solid hydrates of nitric acid: Implications for polar stratospheric clouds, *Science*, 259, 70, 1993.

2-D MAGI: Two-Dimensional Modeling of Aircraft Global Impacts

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Research Objectives

This research project emphasizes the application of the LLNL 2-D chemical-radiative-transport model to determining the impact of present and potential future aircraft emissions on the global atmosphere. The intention is to reduce uncertainties and better define the range of possible effects of aircraft emissions on the atmosphere. Realistic scenarios for aircraft emissions are examined to evaluate past as well as future effects on the atmosphere. Further development and improvement of the model will be done to meet the special needs of the HSRP program with special consideration on understanding the effect of heterogeneous chemistry on changing the chemical species partitioning in the stratosphere.

Summary of Progress and Results

The LLNL two-dimensional model has been used to assess the impact of proposed 2015 subsonic and HSCT emissions on ozone and other trace gases. Results from this effort are in the NASA HSRP/AESA 1993 (Ko *et al.*, 1993) assessments of the Atmospheric Effects of Stratospheric Aircraft.

We have continued our investigation of the dynamical transport in the LLNL 2-D model by using carbon-14 and strontium-90 as inert tracers of stratospheric motion. We submitted results of this study, which is a collection of our recent work plus a reduced version of the manuscript from the work published in Section I, *The Atmospheric Effects of Stratospheric Aircraft: Report of the 1992 Models and Measurements Workshop*.

There have been a number of improvements to the LLNL two-dimensional model over the last year. Polar heterogeneous chemistry has been added to the LLNL two-dimensional chemical mechanism to investigate the potential effects of NO_x and H₂O emissions from HSCTs during periods when Polar Stratospheric Clouds are formed. We have made major strides in developing fully interactive dynamics for the model. A planetary wave module has been developed and is now being integrated with the rest of the dynamics solver.

Don Wuebbles has continued to chair the Emission Scenarios Committee (Wuebbles *et al.*, 1993a). The outcome of this effort has produced the most comprehensive and realistic analyses to date for emissions from aircraft in 1990 and for 2015 subsonic and HSCT projected emission scenarios. These scenarios were used by the participating global models for the 1993 NASA HSRP/AESA assessment. A journal article is in progress describing the existing emissions database.

Don was also a lead author for the interim assessment report (Albritton *et al.*, 1993) prepared for the National Research Council. His chapter (Wuebbles *et al.*, 1993b) concerned the findings on fleet operational scenarios and the emissions database described above.

Don has also represented NASA HSRP/AESA for the Global Emissions Inventory Activity (GEIA), International Global Atmospheric Chemistry (IGAC) Core Project of the International Geosphere-Biosphere Program (IGBP). A summary report was published on this effort (Wuebbles, 1993). Also for NASA, Don Wuebbles and Doug Kinnison have participated in the International Civil Aviation Organization (ICAO), Emission Inventory Sub Group (EISG), evaluation of past, present, and future subsonic emissions.

Publications

- Albritton, D. L., W. H. Brune, A. R. Douglass, F. L. Dryer, M. K. W. Ko, C. E. Kolb, R. C. Miake-Lye, M. J. Prather, A. R. Ravishankara, R. B. Rood, R. S. Stolarski, R. T. Watson, and D. J. Wuebbles, *The Atmospheric Effects of Stratospheric Aircraft: Interim Assessment Report of the NASA High-Speed Research Program*, NASA Reference Publication 1333, 1993.
- Kinnison, D. E., H. S. Johnston, and D. J. Wuebbles, Model study of atmospheric transport using carbon-14 and strontium-90 as inert tracers, *J. Geophys. Res.*, 99, 20647, 1994.
- Ko, K. W., and A. R. Douglass, Update of model simulations for the effects of stratospheric aircraft, Chapter 4, in *The Atmospheric Effects of Stratospheric Aircraft: A Third Program Report*, M. J. Prather and H. L. Wesoky, editors, NASA Reference Publication 1313, 1993.
- Wuebbles, D. J., *Project Report: Aircraft*, Fourth International Workshop on Global Emissions Inventories, Summary Report, Global Emissions Inventory Activity, International Global Atmospheric Chemistry Program, November 30-December 2, Boulder, CO, 1993.
- Wuebbles, D. J., D. Maiden, R. K. Seals Jr., S. L. Baughcum, M. Metwally, and A. K. Mortlock, Emissions scenarios committee report, Chapter 3, in *The Atmospheric Effects of Stratospheric Aircraft: A Third Program Report*, M. J. Prather and H. L. Wesoky, editors, NASA Reference Publication 1313, 1993.
- Wuebbles, D. J., S. L. Baughcum, M. Metwally, and R. K. Seals Jr., Fleet operational scenarios, in *The Atmospheric Effects of Stratospheric Aircraft: Interim Assessment Report of the NASA High-Speed Research Program*, R. S. Stolarski and H. L. Wesoky, editors, NASA Reference Publication 1333, 1993.

Ancillary Measurements and Mission Support for SPADE

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Research Objectives

The first objective of this project is to assist in developing a chemical trajectory model for SPADE by providing SAGE II observations of aerosol extinction and SAGE II deduced aerosol composition and surface area. The second objective of this project is to compare SPADE measurements of aerosol surface area, ozone mixing ratio, and water vapor mixing ratio with SAGE II measurements and/or SAGE II climatology of aerosols and trace gases.

Summary of Progress and Results

SAGE II observations of aerosol extinction at 1.02 micron in 1993 were utilized to generate curtains (profiles) of aerosol extinction along the trajectory. These curtains were incorporated into the GUMBO model which is being developed as part of the SPADE program. In addition, curtains of aerosol surface area and composition along the trajectory were also produced.

Water vapor profiles obtained with a Lyman Alpha hygrometer during the SPADE campaign were compared with the average profiles obtained by SAGE II from 1986 to 1990. It was found that the SAGE II water vapor mixing ratios around the tropopause are lower than the Lyman-Alpha measurements. With the exception of one profile, tropospheric water vapor concentrations measured by the Lyman-Alpha during SPADE were in reasonably good agreement with the average SAGE II values.

When SAGE II deduced aerosol surface areas were compared with measurements by the Forward Scattering Spectrometer Probe (FSSP) during the SPADE campaign, agreement was quite good in some cases. For other cases, SAGE II surface areas were higher than the FSSP measurements at 18-20 km, but agreed reasonably well with FSSP measurements at lower altitudes.

An empirical time-series model for estimating ozone mixing ratios based on SAGE II monthly mean ozone data for the period October 1984 through June 1991 has been developed. Ozone profiles obtained by a Dual-Beam UV-Absorption ozone photometer during the SPADE campaign were compared with the model results. With the exception of two profiles at altitudes below 16 km, ozone mixing ratios derived by the model and measured by the ozone photometer were in agreement to within their individual uncertainties.

Publications

Kinnison, D. E., H. S. Johnson, D. K. Weisenstein, and G. K. Yue, Radionuclides as exotic tracers, Section I, in *The Atmospheric Effects of Stratospheric Aircraft: Report of the 1992 Models and Measurements Workshop*, Vol. III, M. J. Prather and E. E. Remsberg, editors, NASA Reference Publication 1292, 1993.

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- Yue, G. K., L. R. Poole, P.-H. Wang, and E. W. Chiou, Aerosol acidity, density and refractive index deduced from SAGE II and NMC temperature data, *J. Geophys. Res.*, *99*, 3727-3738, 1994.
- Yue, G. K., L. W. Thomason, L. R. Poole, P.-H. Wang, D. Baumgardner, and J. E. Dye, Aerosol surface area deduced from early 1993 SAGE II data and their comparisons with Stratospheric Photochemistry, Aerosols and Dynamics Expedition measurements, submitted to *Geophys. Res. Lett.*
- Yue, G. K., J. M. Zawodny, L. R. Poole, R. E. Veiga, and M. H. Proffitt, Estimated SAGE II ozone mixing ratios in early 1993 and comparisons with Stratospheric Photochemistry, Aerosols and Dynamics Expedition measurements, *Geophys. Res. Lett.* *21*, 2607-2610, 1994.

Appendix A

HSRP/AESA Fourth Program Report Reviewers

Appendix A
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16. Abstract This document presents the fourth report from the Atmospheric Effects of Stratospheric Aircraft (AESA) component of NASA's High-Speed Research Program (HSRP). Market and technology considerations continue to provide an impetus for high-speed civil transport research. A recent AESA interim assessment report and a review of that report have shown that considerable uncertainty still exists about the possible impact of aircraft on the atmosphere. The AESA has been designed to develop the body of scientific knowledge necessary for the evaluation of the impact of stratospheric aircraft on the atmosphere. The first Program report presented the basic objectives and plans for AESA. This fourth report comes after the interim assessment and sets forth directions for the 1995 assessment at the end of AESA Phase I. It also sets forth the goals and directions for AESA Phase II, as reported at the 1994 Atmospheric Effects of Aviation Project (AEAP) annual meeting held in June. The focus of the Phase II effort is to obtain the best possible closure on the outstanding problems identified in the interim assessment and NASA/NRC review. Topics discussed in this report include how high-speed civil transports (HSCT) might affect stratospheric ozone, emissions scenarios and databases to assess potential atmospheric effects from HSCTs, calculated results from 2-D zonal mean models using emissions data, engine trace constituent measurements.					
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